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THE CONSTITUTION OF ALUMINIUM-COPPER-MAGNESIUM ALLOYS.*

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(Contribution from the Research Laboratories of The British Aluminium Co., Ltd.)

SYNOPSIS.

The constitution of the aluminium-rich ternary alloys of aluminium, copper, and magnesium has been investigated over the range 0–40% copper, 0–35% magnesium by methods of thermal analysis and microscopic examination. Most attention has been paid to the structures of the alloys as slowly solidified, but one isothermal section (at 430° C.) has been studied under conditions of equilibrium.

The occurrence of the two binary constituents, CuAl_2 and Mg_2Al_3 , and of two ternary compounds, $S(\text{Al}_2\text{CuMg})$ and $T(\text{Al}_3\text{CuMg}_4)$, has been confirmed. The liquidus surface contains three ternary invariant points:

Eutectic; $\text{Al}, \text{CuAl}_2, S$: 33.0% Cu, 6.1% Mg; 507° C.

Peritectic; $\text{Al}, S \rightarrow T$: 26.0% Mg, 10.0% Cu; 467° C.

Eutectic; $\text{Al}, T, \text{Mg}_2\text{Al}_3$: 2.7% Cu, 32.0% Mg; 451° C.

The peritectic reaction between liquid and S giving rise to T rarely proceeds to completion during solidification, ceasing almost as soon as the S crystals have become enveloped by a sheath of T .

Although under equilibrium conditions the system $\text{Al}-S$ appears to be quasi-binary, under conditions likely to be met with in industrial practice a small excess of magnesium over that required to form Al_2CuMg is necessary in order to ensure complete suppression of CuAl_2 .

It is shown that the liquidus isothermals of the primary S and T fields follow reasonably well the respective mass-action laws $[\text{Cu}][\text{Mg}] = \text{constant}$ and $[\text{Cu}][\text{Mg}]^4 = \text{constant}$.

Work on the solid solubility of copper and magnesium has been confined to the re-investigation of points on which the results of previous investigations are divergent. Confirmatory evidence is brought forward to show that at 430° C. the apex of the three-phase field ($\text{Al} + \text{CuAl}_2 + S$) lies at 2.2% Cu, 1.0% Mg and therefore very close to the $\text{Al}-S$ line; that the apices of the fields ($\text{Al} + S + T$) and ($\text{Al} + T + \text{Mg}_2\text{Al}_3$) lie close to the $\text{Al}-\text{Mg}$ axis, having co-ordinates approximately 0.23% Cu, 9.2% Mg and 0.16% Cu, 10.2% Mg; and that Mg_2Al_3 is capable of dissolving copper to the extent of about 2.5%.

I.—INTRODUCTION.

THIS investigation is one of a series,¹ the chief purpose of which is to obtain some insight into the constitution of aluminium-rich alloys

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under conditions of metastable equilibrium likely to be met with in industrial practice. As in previous investigations, most attention has been paid to those alloys in which aluminium is the primary constituent to separate on solidification, but the survey has been extended a small distance into the adjoining primary-phase fields so as to permit of a study being made of their initial slopes. No attempt has been made to study the equilibrium structures over a wide range of temperatures and compositions, and work has been confined to the investigation of the extreme aluminium corner at one particular temperature, in order to obtain independent evidence on points on which published information is conflicting.

Many commercial aluminium alloys contain copper and magnesium as essential alloying constituents. In addition, they contain silicon and iron, either as incidental impurities or as controlled additions, and very frequently they contain other elements such as manganese or nickel. One of the most important of these is Duralumin, which was developed by Wilm² in 1909, and shown to possess remarkable age-hardening properties. Alloys of the same type are in widespread use to-day, the copper content ranging from 2.5 to 5% and the magnesium from 0.2 to 1.5%, with manganese 0.3 to 1.5%. Among the constituents which may be present in these more complex alloys are those of the aluminium-copper-magnesium ternary system, so that a knowledge of the constitution of the latter is essential to an understanding of the structure of the complex industrial alloys. Nothing has hitherto been published on the constitution of the alloys under the conditions of metastability likely to be encountered in industrial practice.

II.—HISTORICAL SURVEY.

The constitution of the ternary system aluminium-copper-magnesium under equilibrium conditions has been the subject of numerous investigations, the more recent of which are in agreement as regards the number of phases occurring and the reactions taking place during solidification and annealing. There are still some differences of opinion about the limits of occurrence of the various phases, and about the chemical formulæ to be assigned to some of them. Until recently there has been no uniformity of nomenclature in describing the structures: different letters have been used to indicate the same phases. In describing previous work a uniform system of terminology will be adopted, and the account will be prefaced by a brief review of the constitution under equilibrium conditions as now commonly accepted.

It is now generally agreed that in the neighbourhood of the

aluminium corner of the system, the constituents which may exist in equilibrium with the aluminium-rich solid solution are the two binary bodies, CuAl_2 (often termed θ) and Mg_2Al_3 (β), and two ternary bodies which may be termed S and T , and for which the formulæ Al_2CuMg and Al_6CuMg_4 may be taken as established. To conform with the system of nomenclature used in previous papers of this series, these two ternary bodies should be designated $\alpha(\text{CuMg})$ and $\beta(\text{CuMg})$, respectively: the use of the letters S and T is, however, widely accepted

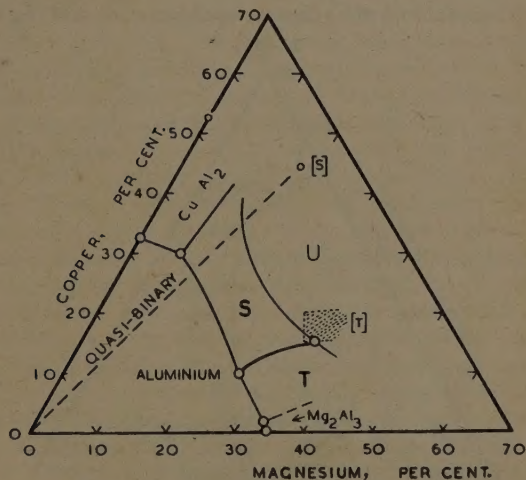


FIG. 1.—The Liquidus Surface (Urazov and Petrov).

and it seemed better to adhere to it. The system $\text{Al}-S$ is quasi-binary, and divides the aluminium corner of the ternary system into two partial ones in which the phases present are (i) $\text{Al}-\text{CuAl}_2-S$, and (ii) $\text{Al}-S-T-\text{Mg}_2\text{Al}_3$. The dividing line between the two partial systems is thus that along which the ratio of copper to magnesium is equi-atomic, or 2.6 : 1 in percentage by weight.

The liquidus surface is shown in Fig. 1.

The primary aluminium phase field is separated by eutectic valleys from the adjoining fields, in which the primary constituents are CuAl_2 , S , T , and Mg_2Al_3 . The partial system $\text{Al}-\text{CuAl}_2-S$ is a simple eutectiferous one, with a ternary eutectic lying at approximately 33% Cu , 6.1% Mg and freezing at 507°C . In the other partial system there is a ternary eutectic of Al , T , and Mg_2Al_3 , containing approximately 2.7%

Cu, 32% Mg, and freezing at 451°C ., the temperature thus being identical, within the limits of experimental error, with that of the binary eutectic of aluminium and Mg_2Al_3 . Over a wide range of compositions, T is formed peritectically from S and liquid, the invariant point at which Al, S , and T are in equilibrium with the liquid lying at approximately 26% Cu, 10% Mg, 467°C . In alloys rich in copper and magnesium, S and T do not separate directly from the liquid, but are formed as the result of a peritectic reaction between a constituent termed U and the liquid.

The constitution of the alloys in equilibrium at 400°C . is shown in Fig. 2.

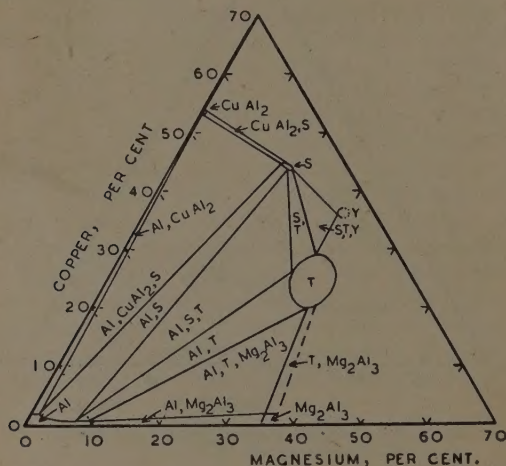


FIG. 2.—Isothermal Section : 400°C . (Hume-Rothery, Petrov).

Surrounding the aluminium corner there is a small field in which the aluminium-rich solid solution is the only constituent present. CuAl_2 , which has a small homogeneity range in binary aluminium-copper alloys, is practically incapable of dissolving magnesium. S has a small, and T a relatively large homogeneity range, while the solid solubility of copper in Mg_2Al_3 is of the order of 2.5%. The remainder of the diagram is divided into fields in which two or three phases are in equilibrium, and which do not require detailed comment at this stage.

In colour, crystal habit, hardness, and etching behaviour, CuAl_2 and S are not very different, and it is not surprising that, in the earliest

investigations, the distinction between them was not recognized. Thus Vogel,³ who was the first to make a systematic investigation of the ternary alloys, believed that CuAl_2 was capable of taking a considerable quantity of magnesium into solid solution, and drew the Al-CuAl_2 eutectic valley as running from the binary eutectic to the invariant point at 10% Cu, 27% Mg at which, it is now known, the solid phases in equilibrium with the liquid are Al, S , and T . He discovered the existence of the ternary phase now designated T , giving it the formula Al_6CuMg_4 , and placed the ternary eutectic of Al, T , and Mg_2Al_3 very close to the aluminium-magnesium axis. He showed the T field as rising to a low maximum. His findings, together with those of later workers on the liquidus invariant points, are given in Table I. Ohtani⁴ did not distinguish between CuAl_2 and S , or between Mg_2Al_3 and T : he believed that CuAl_2 and Mg_2Al_3 formed a continuous series of solid solutions, the primary field of which was separated from the aluminium field by a continuous valley running from the one binary eutectic to the other. Gayler,⁵ who investigated the isothermals below the solidus, accepted Vogel's diagram, and also did not discover the distinction between CuAl_2 and S . The positions she found for the boundaries of the 2-phase and 3-phase fields involving the T constituent are almost identical with those reported within the last few years by Petrov and Berg, and are included, with other data on the isothermals below the solidus, in Table II. Dix, Sager, and Sager⁶ determined the effect on the solidus temperature and on the solid solubility of CuAl_2 of adding 0.5% magnesium to binary aluminium-copper alloys. Their findings are consistent with recent work by Hume-Rothery and his colleagues. Portevin and Bastien,⁷ studying the magnesium-rich alloys of the system, carried their investigations sufficiently far towards the aluminium corner to identify a ternary phase to which they assigned the formula $\text{Al}_2\text{Cu}_3\text{Mg}_2$, and which may be the phase U involved in the peritectic reactions giving rise to the phases S and T .

During the years 1934-36, several papers were published by Laves and his co-workers on the crystal structures of the ternary phases of the system. Laves and Löhberg⁸ identified the compound AlCuMg and found it to be isomorphous with MgZn_2 . It crystallizes in the hexagonal system, with $a = 5.09$, $c = 8.35$ kX., the space group being $D_{6h}^{4h}-C6/mmc$. Laves, Löhberg, and Witte⁹ confirmed the existence of Al_6CuMg_4 (the T phase), reporting it to be cubic and isomorphous with $\text{Al}_2\text{Mg}_3\text{Zn}_3$. Laves and Witte¹⁰ found that the solubility of magnesium in CuAl_2 was not large, as Vogel had stated, but was in fact extremely small, and that a ternary phase existed, to which they gave the formula $\text{Al}_6\text{Cu}_2\text{Mg}_2$. This is the phase now designated S . They

also discovered another ternary compound, to which they assigned the formula $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$, and confirmed the existence of AlCuMg . They disputed the existence of $\text{Al}_2\text{Cu}_3\text{Mg}_2$, which they considered to be a member of an extensive series of solid solutions. Laves and Werner¹¹ found that $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$ crystallized in the cubic system, with $a = 8.29$ kX., the unit cell containing 82 atoms. The existence of the phase now known as *S* was confirmed in 1937 by Schütz,¹² who used the methods of thermal analysis. He suggested, however, that the appropriate formula was $\text{Al}_{11}\text{Cu}_4\text{Mg}_4$, and not $\text{Al}_5\text{Cu}_2\text{Mg}_2$.

An extensive study of the system was made in 1937 by Nishimura,¹³ whose diagram is almost identical with that plotted in Fig. 1. He established the quasi-binary nature of the system Al-*S*, and showed that the binary valley between the Al and *S* fields rose to a maximum (510° C.) at its point of intersection with the quasi-binary line. He assigned the formula $\text{Al}_{13}\text{Cu}_7\text{Mg}_8$ to the phase *S*, and Al_5CuMg_4 to *T*. He showed that, over a certain range of compositions, *S* and *T* were formed peritectically from a compound (*U*) richer in copper and magnesium, the composition of which he did not determine. His values for the invariant points are included in Table I. The quasi-binary character of the system Al-*S* was confirmed in the following year by Petrov,¹⁴ who reported that the system CuAl_2 -*S* was also quasi-binary.

In 1940 Kuznetsov and Guseva¹⁵ published the results of an investigation on reactions below the solidus, in which they covered the temperature range 200°–445° C. The positions of the various phase boundaries, which were determined from changes of the slope of the curves connecting lattice parameter with composition, differ somewhat from those plotted in Fig. 2, the chief difference being that the line separating the aluminium from the (Al + *S*) and (Al + *T*) fields is drawn parallel to the aluminium-magnesium axis, and at a constant distance from it equivalent to about 0.6% magnesium, irrespective of the temperature. More detailed results are included in Table II. In the following year Obinata and Mutuzaki¹⁶ published the results of an X-ray study of the crystal structure of the phase *S*. They gave its composition as $\text{Al}_5\text{Cu}_2\text{Mg}_2$, and stated that it crystallized in the tetragonal system, with parameters $a = 5.71$, $c = 7.94$ kX., and with 18 atoms in the unit cell. These findings were, however, not confirmed by Perlitz and Westgren,¹⁷ who reported that the nearest formula was Al_2CuMg , and that the lattice was face-centred orthorhombic, with 16 atoms in the unit cell. Guertler and Rassmann¹⁸ also made a study, by X-ray methods, of the intermetallic compounds, and of the systems formed by these bodies taken in pairs. They identified $\text{Al}_5\text{Cu}_2\text{Mg}_2$ (*S*) and Al_6CuMg_4 (*T*), and confirmed that these constituents

formed quasi-binary systems with CuAl_2 and Mg_2Al_3 respectively, with aluminium, and with each other. Of compounds richer in copper and magnesium, they claimed to have identified $\text{Al}_{11}\text{Cu}_{11}\text{Mg}_4$ and AlCuMg , the former being the phase to which Laves and Witte gave the formula $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$.

The isothermal section at 460°C . was studied over a wide range of compositions in 1944 by Little, Hume-Rothery, and Raynor,¹⁹ and some determinations were made over a limited range at 375°C . They confirmed that CuAl_2 has only a very limited capacity for dissolving magnesium at this temperature, placing the limit below 0.1%, and showed that the aluminium apex of the three-phase triangle $\text{Al-CuAl}_2\text{-S}$ follows the equi-atomic line very closely with falling temperature. They also determined the homogeneity ranges of the constituents S and T , which they showed could be represented fairly closely by the formulæ Al_2CuMg and Al_6CuMg_4 . They found that the Al-S solid-solubility curve obeyed the mass-action law:

$$[\text{Cu}] \times [\text{Mg}] = K$$

where square brackets denote concentrations in atomic percentages and K is a constant, and they further showed that the change of solubility product with temperature could be represented by the equation:

$$\log_{10} K = A - \frac{B}{\theta}$$

where A and B are constants, and θ the absolute temperature. Their results have been used to a considerable extent in plotting Fig. 2.

Two comprehensive papers were published in 1946 by Russian investigators. The earlier paper, by Urazov and Petrov,²⁰ covered a re-determination of the liquidus surface over a wide range of compositions. Their diagram, which is in close agreement with Nishimura's, has been used in drawing Fig. 1. The chief differences between the two investigations lie in the formulæ assigned to the ternary constituents: the Russians, like Perlitz and the Oxford investigators, consider S to be Al_2CuMg , and they follow Vogel in assigning the formula Al_6CuMg_4 to T . They state that the phase U , involved in the peritectic reactions giving rise to S and T , can be represented well by the formula $\text{Al}_2\text{Cu}_4\text{Mg}_3$. The second paper, in which Petrov collaborated with Berg,²¹ dealt with isothermals below the solidus. The positions which they gave for the phase boundaries in magnesium-rich alloys agree well with those found by Gayler, but in the copper-rich alloys they place the aluminium apex of the $\text{Al-CuAl}_2\text{-S}$ field much nearer to the aluminium-copper axis than do Hume-Rothery and his colleagues. Petrov and Berg also investigated the homo-

geneity ranges of *S* and *T*. In the case of *S*, their findings agree very closely with those of the Oxford school, but in the case of *T*, the two schools are not in agreement. The differences can best be appreciated from a comparison between Figs. 1 and 2: in the former Petrov and Berg's values for the limits of *T* have been inserted, in the latter, those of Hume-Rothery and his colleagues. Petrov and Berg report that the three-phase field lying beyond the (*S* + *T*) field contains (*U* + *S* + *T*), in which *U* has the formula $\text{Al}_2\text{Cu}_4\text{Mg}_3$, whereas in a paper published in 1947, Strawbridge, Hume-Rothery, and Little²² show this field as (*Y* + *S* + *T*), with *Y* having a composition approximately given by the formula $\text{Al}_7\text{Cu}_3\text{Mg}_6$. The latter formula is based on a very extensive study of the phase fields lying on the copper side of the CuAl_2 -*S* and *S*-*T* quasi-binary systems, and appears to be the better authenticated. The ternary constituents identified by Hume-Rothery and his colleagues, in addition to *S*, *T*, and *Y*, were *Z* (approximately $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$), and *M* (approximately AlCuMg).

The co-ordinates of the invariant points of the liquidus surface, as reported by previous investigators, are given in Table I.

TABLE I.—*The Liquidus Surface.*

Investigator :	Vogel.	Nishimura.	Urazov & Petrov.
Reference :	3	13	20
Ternary eutectic $\text{Al-CuAl}_3\text{-S}$	not detected	27% Cu 5% Mg 500° C.	29.7% Cu 7.2% Mg 500° C.
Maximum on <i>Al-S</i> valley	not detected	510° C.	512° C.
Peritectic <i>Al-S-T</i>	10% Cu 27% Mg 471° C.	12% Cu 25% Mg 465° C.	10% Cu 25.6% Mg 465° C.
Ternary eutectic $\text{Al-T-Mg}_2\text{Al}_3$	~0% Cu 35% Mg 451° C.	2% Cu 33% Mg 447° C.	1.5% Cu 33% Mg 445° C.
Peritectic <i>U-S-T</i>	not detected	14% Cu 31% Mg 525° C.	15% Cu 34% Mg 525° C.

A summary of data on structures below the solidus is given in Table II. It has been considered sufficient to list the co-ordinates of the aluminium corners of the three-phase triangles at various temperatures. Values have been obtained by interpolation or extrapolation in cases where the temperatures listed were not those at which

the original observations were made. Changes in the homogeneity limits of the intermetallic phases with falling temperature seem to be negligibly small, so that the boundaries of the fields can be obtained by drawing straight lines from these limits to the appropriate aluminium corners.

TABLE II.—*Isothermals below the Solidus.*

Temp., °C.	Observer.	Reference.	Apex Al-CuAl ₃ -S.		Apex Al-S-T.		Apex Al-T-Mg ₂ Al ₃ .	
			Cu, %	Mg, %	Cu, %	Mg, %	Cu, %	Mg, %
500°	Nishimura	13	3.5	0.5
	Hume-Rothery	19, 22	3.9	1.5
	Petrov	21	3.6	0.8
445°	Nishimura	13	3.0	0.3	0.2	6.0	0.2	8.5
	Kuznetsov	15	2.8	0.7	0.6	7.5	0.6	14.3
	Hume-Rothery	19, 22	2.5	1.1	0.2	9.0
	Petrov	21	2.0	0.6	0.3	8.5	0.3	10.5
400°	Gayler	5	0.4	8.0	0.4	8.5
	Nishimura	13	2.5	0.2	0.2	5.0	0.2	7.0
	Kuznetsov	15	1.7	0.4	0.6	6.2	0.6	10.3
	Hume-Rothery	19, 22	1.7	0.8
	Petrov	21	1.4	0.4	0.3	7.4	0.2	9.5
300°	Gayler	5	0.4	6.5	0.4	7.3
	Nishimura	13	2.5	0.2	0.2	4.0	0.2	5.0
	Kuznetsov	15	0.8	0.3	0.6	4.3	0.6	5.0
	Hume-Rothery	19, 22	0.5	0.3
	Petrov	21	0.6	0.2	0.1	5.0	0.1	5.6

Table III shows the formulæ which have been assigned from time to time to the various ternary constituents, and also the formulæ which appear to be the best authenticated. Compositions corresponding to the latter do not necessarily lie within the homogeneity range of the constituents in question.

TABLE III.—*Formulæ Assigned to Ternary Constituents.*

Observer.	Reference.	S	T	U	Higher Compounds.	
Vogel	3	...	Al ₃ CuMg ₃
Portevin	7	...	Al ₃ CuMg ₃	Al ₂ Cu ₃ Mg ₃
Laves, Löbberg, Witte	8, 9, 10	Al ₃ Cu ₂ Mg ₃	Al ₃ CuMg ₃	...	AlCuMg	Al ₁₀ Cu ₃ Mg ₃
Schütz	12	Al ₁₁ Cu ₃ Mg ₃
Nishimura	13	Al ₁₁ Cu ₃ Mg ₃	Al ₃ CuMg ₃
Obinata	16	Al ₃ Cu ₂ Mg ₃
Perlit	17	Al ₃ CuMg ₃
Guertler	18	Al ₃ Cu ₂ Mg ₃	Al ₃ CuMg ₃	...	AlCuMg	Al ₁₁ Cu ₁₁ Mg ₃
Petrov	20, 21	Al ₃ CuMg ₃	Al ₃ CuMg ₃	Al ₂ Cu ₃ Mg ₃
Hume-Rothery	19, 22	Al ₃ CuMg ₃	Al ₃ CuMg ₃	Al ₃ Cu ₃ Mg ₃	AlCuMg	Al ₁₀ Cu ₃ Mg ₃
Best authenticated	Al ₂ CuMg	Al ₃ CuMg ₃	Al ₃ Cu ₃ Mg ₃	AlCuMg	Al ₁₀ Cu ₃ Mg ₃

III.—EXPERIMENTAL DETAILS.

1. *Preparation of Alloys.*

For the initial survey, series of alloys were prepared of which the composition varied in steps of 2% within the range 0–10% Cu, 0–10% Mg, and in steps of 5% outside that range. When a phase boundary had been approximately located, additional alloys were made up first in steps of 1% and finally in steps of 0.25%. Two ranges of alloys were investigated, one 0–40% Cu, 0–12% Mg, and the second 0–25% Cu, 12–35% Mg, thus leaving the higher portions of the *S* field unexplored. Aluminium of purity 99.91% was used for the preliminary stages of the investigation, and super-purity aluminium for the detailed work, the analyses being:

Aluminium, %	99.91	99.995
Silicon, %	0.06	0.0030
Iron, %	0.03	0.0015
Copper, %	<0.005	<0.001
Manganese, %	<0.005	<0.001

Copper was added in the form of a 50% hardener, while magnesium was added either as such, or as a 10% hardener, carnallite being used as a flux. Typical analyses of the hardeners, and of two of the alloys, are as follows, and serve to indicate the general level of contamination:

	Copper Hardener.	Magnesium Hardener.	Nominal, 3.5% Cu, 1.0% Mg.	Nominal, 1% Cu, 34% Mg.
Aluminium, %	49.89	90.00	95.62	65.22
Copper, %	50.10	<0.001	3.40	0.97
Magnesium, %	nil	9.99	0.97	33.80
Silicon, %	0.0030	0.0035	0.0040	0.007
Iron, %	0.0025	0.0050	0.0015	0.002
Manganese, %	<0.001	<0.001	<0.001	<0.001

For cooling curves, quantities of about 200 g. were taken, and the rate of cooling was, in general, about 8° C./min. This rate of cooling was identical with that used in previous investigations, and was originally chosen as being intermediate between that likely to occur in chill casting and that in sand casting. Temperatures were measured by a platinum/platinum-rhodium thermocouple, calibrated against the boiling point of water and the melting points of tin, lead, zinc, aluminium, and copper, and used in conjunction with a Carpenter-Stansfield potentiometer. Very thorough stirring, up to the commencement of solidification, was found to be essential if effects due to segregation were to be avoided.

For annealing below the solidus, samples were prepared in the

form of thin chill-cast bars, and were polished for microscopic examination before annealing. At the temperature selected, 430° C., equilibrium appeared to have been reached within 14 days.

2. Chemical Analysis.

Copper, if present in amounts not exceeding 0.25%, was estimated colorimetrically by means of sodium diethyl dithiocarbamate.²³ In the range 0.25–25% the estimation was made volumetrically, using thio-sulphate,²⁴ while for still higher contents, up to 40%, the electrolytic method was used.²⁵ For magnesium, if present in amounts less than 5%, the oxine method was used, with a volumetric finish.²⁶ For contents in excess of 5%, the pyrophosphate method was employed.²⁷ The small quantities of silicon and iron present as incidental impurities were estimated colorimetrically; the former, after removal of copper, by matching the yellow colour developed by ammonium molybdate in acid solution against standard picric acid,²⁸ and the latter, after removal of the copper, by the thiocyanate process.²⁹ The small amount of manganese present as impurity was estimated colorimetrically, periodate being used as the oxidizing agent.³⁰

IV.—MICROGRAPHY OF THE ALLOYS.

Specimens for microscope examination were ground by hand as far as No. 00 emery, and afterwards polished on a rotating cloth-covered wheel with levigated alumina as the abrasive. The final polish was given by hand, with "Silvo" metal polish on Selvyt cloth. Freshly ignited magnesia was tried for the two finishing stages, but appeared to offer no advantages. Various modifications of the electrolytic-polishing methods advocated by Jacquet³¹ and by de Sy and Haemers³² were also tried, but were not found to be satisfactory owing to the very high relief shown by the intermetallic constituents.

The aluminium-rich solid solution, usually showing pronounced coring, forms the continuous phase over the greater part of the range studied. The addition of copper to aluminium causes a contraction of the lattice, the relationship being linear, while the addition of magnesium causes an expansion,^{15, 33} the relationship being linear with quantities of magnesium in excess of about 2% but curved below this percentage. From the data published by Kuznetsov and Guseva,¹⁵ it would appear that in the ternary alloys the effects of copper and magnesium are additive, and that the linear relationship is retained. The line along which the contraction due to the copper is counter-balanced by the expansion due to the magnesium lies slightly on the

magnesium side of the quasi-binary line Al-S. Figures for the lattice parameter of the solid solution, measured at room temperature, have been compiled from various sources and are given in Table IV. They refer to aluminium which has been brought into equilibrium with the phases specified by annealing at 445° C., and retained in a condition of supersaturation by quenching.

TABLE IV.—*Lattice Spacings of Saturated Solutions of Copper and Magnesium in Aluminium (Saturation Temperature 445° C.).*

Solid Solution.	Composition.			Lattice Parameter at 20° C.	
	Cu, %	Mg, %	Source : Reference.	kX.	Source : Reference.
Super-purity aluminium	4.0413	33
Al in equilibrium with CuAl_2 .	2.9	...	15, 34	4.035	15, 33
Al in equilibrium with CuAl_2 + S	2.6	1.1	19	4.041	15
Al in equilibrium with S + T .	0.2	9.5	21	4.088	15
Al in equilibrium with T + Mg_2Al_3 .	0.1	12.0	21	4.115	15
Al in equilibrium with Mg_2Al_3	15.5	34	4.118	15

The intermetallic constituents present in the range of compositions studied fall into two groups. CuAl_2 and S are similar in habit, colour, and etching behaviour, and are easily visible in unetched specimens. T and Mg_2Al_3 are also alike in colour, habit, and etching behaviour, and are very difficult to distinguish from the aluminium matrix when unetched. CuAl_2 and S are pink-lilac in colour, S being slightly the darker and often rather more in relief. When primary they adopt a prismatic habit with regular outlines, but in association with aluminium in the eutectic the crystals of both constituents are rounded, and tend to form a lace-like tracery. When etched with sodium hydroxide solution (12½%), both CuAl_2 and S are coloured brown, CuAl_2 being the more reactive. Both are darkened by concentrated nitric acid, or by ferric nitrate solution, and again CuAl_2 is the more reactive. Electrolytic etching in a strongly ammoniacal solution of ammonium molybdate, as used by Gayler ⁵ to distinguish between CuAl_2 , T , and Mg_2Al_3 , can be used to distinguish between CuAl_2 and S , and a simpler electrolyte, consisting of ammonia of specific gravity 0.880, is equally satisfactory. With either electrolyte, S is hardly affected, CuAl_2 is coloured blue, T brown, and Mg_2Al_3 thrown slightly into relief without change of colour. Little, Hume-Rothery, and Raynor ¹⁰ recommend the use of Keller's reagent (10-20 sec. immersion in a solution con-

taining hydrofluoric acid 10, hydrochloric acid 15, and nitric acid 25 ml./l.): this outlines and blackens *S* while leaving CuAl_2 light.

In the unetched condition, *T* and Mg_2Al_3 are very pale grey, almost white in colour. *T* is a little the darker, so that when *T* and Mg_2Al_3 are in association, it is just possible to detect the boundary between them. Primary crystals of *T* tend to be prismatic, but their regular outline is only seen when the secondary phase is Mg_2Al_3 . In association with aluminium, both *T* and Mg_2Al_3 form rounded masses, and eutectic areas of *T* and aluminium often have a sponge-like appearance. Both constituents are outlined, and tinted, on etching with sodium hydroxide solution, but the colours are variable, and range from pink to green, brown, or grey. The attack on *T* is slightly the heavier, so that a light polish, just sufficient to remove the tarnish from Mg_2Al_3 , will leave *T* coloured. Alternatively, after the soda etch the specimen may be given a short immersion in cold concentrated nitric acid. This tends to darken the colour of *T*, and to produce delicate pink or green pastel shades on Mg_2Al_3 . At the eutectic temperature, 451°C ., Mg_2Al_3 is capable of dissolving about 2.5% copper, and while this can be retained in solid solution by quenching, it is readily rejected during slow cooling, and the precipitate of *T* gives rise to a marked Widmanstätten structure.

Crystallographic data on the various intermetallic constituents may be summarized as follows:

CuAl_2 : tetragonal, $a = 6.05$, $c = 4.88$ kX.^{35, 36, 37, 38}

The space group is D_{4h}^{18} — I 4/*mcm*. There are 4 Cu and 8 Al atoms in the unit cell, having the following co-ordinates about the origin and about the body centre:

Cu: $00\frac{1}{4}$; $00\frac{3}{4}$

Al: $x(\frac{1}{2} + x)0$; $\bar{x}(\frac{1}{2} - x)0$; $(\frac{1}{2} + x)\bar{x}0$; $(\frac{1}{2} - x)x0$
with $x = 0.158$

S: orthorhombic, $a = 4.00$, $b = 9.23$, $c = 7.14$ kX.¹⁷

The space group is D_{2h}^{17} — C *mcm*. The co-ordinates of the 16 atoms within the unit cell are:

8 Al: Oyz ; $Oy(\frac{1}{2} - z)$; $\frac{1}{2}(\frac{1}{2} + y)z$; $\frac{1}{2}(\frac{1}{2} + y)(\frac{1}{2} - z)$
 $O\bar{y}\bar{z}$; $O\bar{y}(\frac{1}{2} + z)$; $\frac{1}{2}(\frac{1}{2} - y)\bar{z}$; $\frac{1}{2}(\frac{1}{2} - y)(\frac{1}{2} + z)$
with $y = -0.356$, $z = 0.056$

4 Cu: $Oy\frac{1}{4}$; $\frac{1}{2}(\frac{1}{2} + y)\frac{1}{4}$; $O\bar{y}\frac{3}{4}$; $\frac{1}{2}(\frac{1}{2} - y)\frac{3}{4}$
with $y = -0.22$

4 Mg: as for Cu
with $y = 0.072$.

T: cubic, $a = 14.25$ kX.⁹ The unit cell contains about 160 atoms, but details of the structure are not known.

Mg_2Al_3 : According to Perlitz,³⁹ this is cubic, with $a = 28.13$ kX. The lattice is face-centred, and the space group O_h^2 —*Fd 3m*. The arrangement of the 1172 atoms contained in the unit cell is not known.

V.—THE LIQUIDUS SURFACE.

The liquidus surface, as determined experimentally in the present investigation, is shown in Fig. 3.

In the primary aluminium field, the compositions at which the various isothermals intersect the aluminium-copper axis are almost identical with those published in Raynor's annotated equilibrium diagram,³⁴ but along the aluminium-magnesium axis the intersections agree with those of his diagram only in alloys containing less than 12% magnesium. With higher magnesium contents, the liquidus temperatures were found to be rather lower than those given by Raynor, the discrepancy being about 10° C. at 20–25% magnesium. In the ternary alloys, the isothermals agree, within 5°–10° C., with those that can be drawn by replotting the data published by Nishimura¹³ and by Urazov and Petrov,²⁰ and lead to similar but not quite identical co-ordinates for the various invariant points. The temperature of the $\text{Al-CuAl}_2\text{-S}$ eutectic was determined to be 507° C., and its composition 33.0% Cu, 6.1% Mg. These figures were confirmed by the analysis of portions of several ingots which appeared to consist solely of ternary eutectic. The Al-S-T invariant point was placed at 26% Mg, 10% Cu, and its temperature found to be 467° C. The existence of the peritectic invariant $U\text{-S-T}$, which according to previous investigators should lie at 14–15% Cu, 31–34% Mg, 525° C., could not be confirmed in the present investigation; in fact the constituent *U* was never detected. There were no arrests on the cooling curves which could have been attributed to the separation of primary *U* or to its peritectic conversion into *S* or *T*; and in the microsections no traces of *U* cores in the *S* or *T* crystals were ever detected. It is possible, of course, that the rate of cooling employed was such as to permit the complete conversion of *U* to *S* or *T*, and that the heat evolutions associated with the various reactions were too small to be detected. There was no difficulty in locating the boundary between the *S* and *T* fields: the arrests were well marked, and with rapid cooling the conversion of *S* into *T* was not complete, leading to duplex structures in the micro-sections.

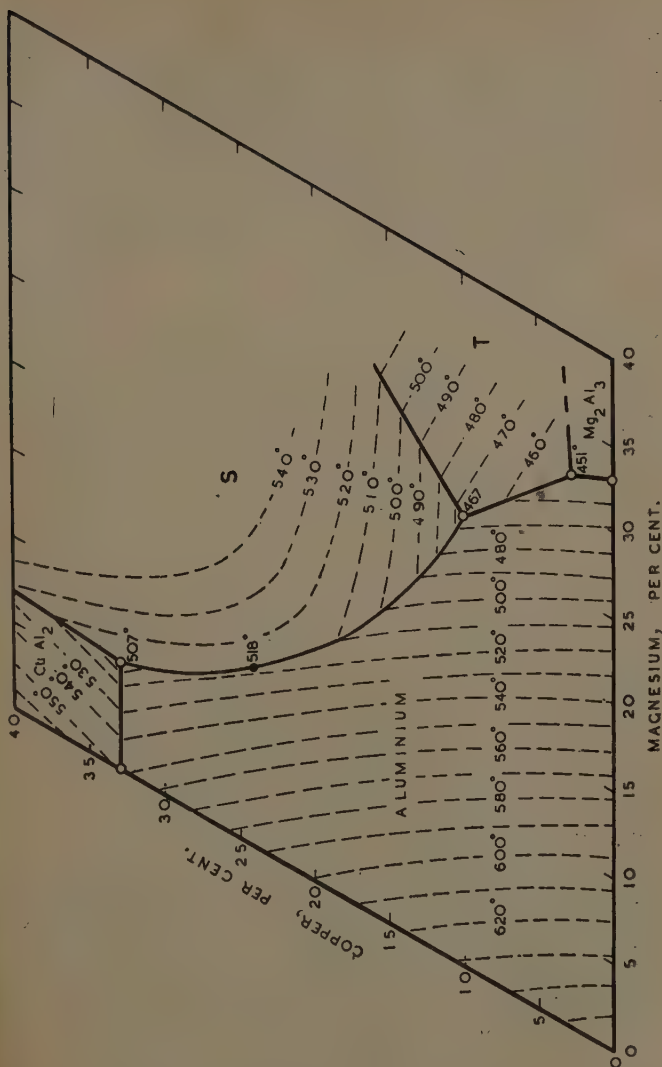


Fig. 3.—The Liquidus Surface.

The co-ordinates of the ternary eutectic $\text{Al-T-Mg}_2\text{Al}_3$ appear to be approximately 2.7% Cu, 32.0% Mg, 451° C., and were determined by preparing several series of alloys with constant magnesium content, and noting the percentage of copper at which *T* became primary. Prolongation of the boundaries between the Al and *T*, and Mg_2Al_3 and *T*, fields to their point of intersection then gave the composition of the eutectic. Several attempts were made to select eutectic portions of ingot for analysis, but consistent results could not be obtained.

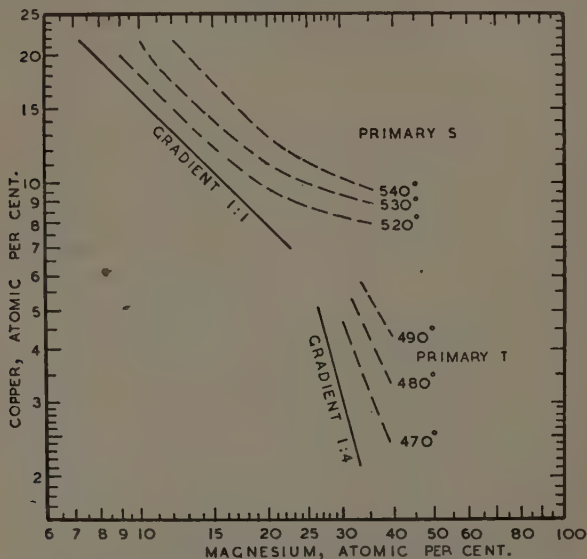


FIG. 4.—Liquidus Isothermals, Primary *S* and *T* Fields (log-log scale).

The solid solubility of copper in Mg_2Al_3 , under the conditions of cooling employed, was approximately 1.6% at the eutectic temperature. Widmanstätten structures, due to precipitation of *T* from supersaturated solid solution, were observed with copper contents as low as 0.25%. Little, Hume-Rothery, and Raynor have shown¹⁹ that the solid-solubility curve Al-*S* follows the mass-action law:

$$[\text{Cu}] \times [\text{Mg}] = \text{constant}$$

It seemed of interest to determine whether the isothermals of the primary *S* field would follow the same law, and therefore observations

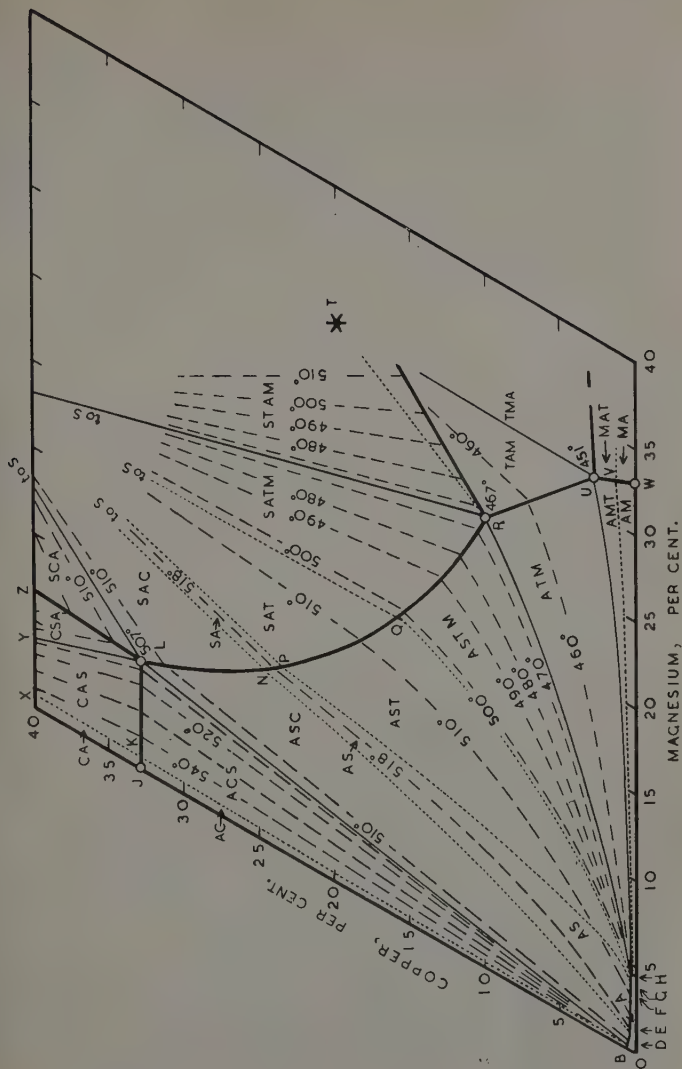


FIG. 5.—Secondary Isothermals.

[To face p. 544.]

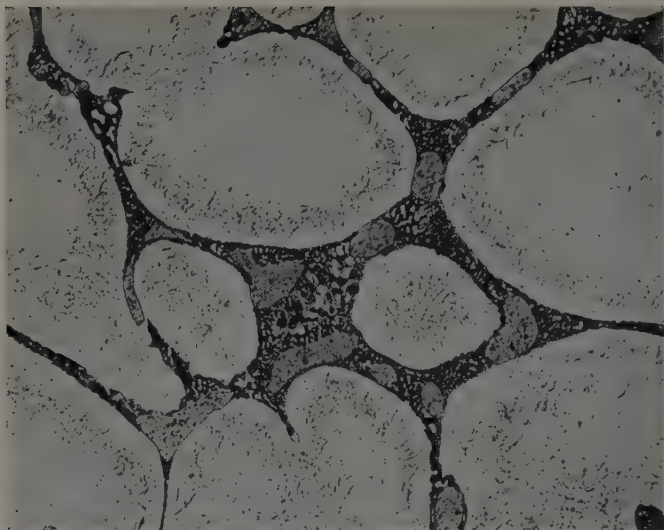


FIG. 6.—Alloy Containing 8% Copper, 2% Magnesium, as slowly solidified. S, grey; CuAl₂, black. Etched with sodium hydroxide followed by ferric nitrate. $\times 300$.

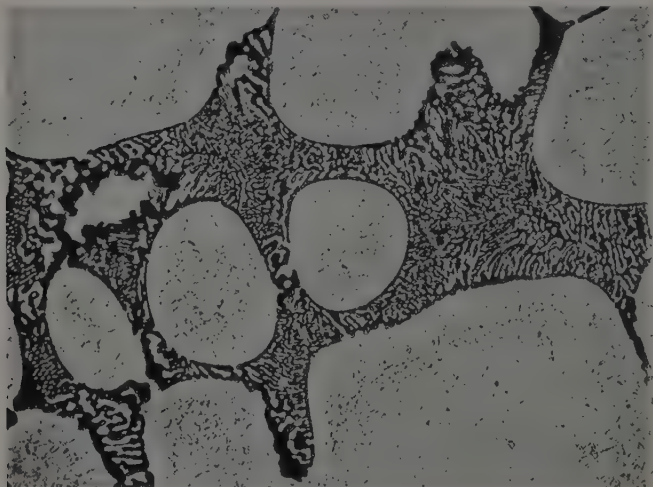


FIG. 7.—Alloy Containing 6% Copper, 4% Magnesium, as slowly solidified. S, black. Etched with ferric nitrate. $\times 300$.

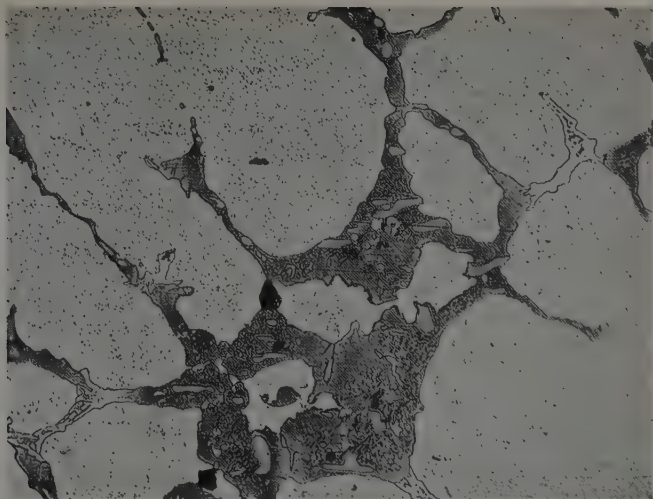


FIG. 8.—Alloy Containing 2% Copper, 10% Magnesium, as slowly solidified. S, grey nodules in darker T; Mg_2Al_3 , white, outlined, and containing precipitated T. Etched with sodium hydroxide and lightly repolished. $\times 200$.



FIG. 9.—Alloy Containing 20% Copper, 20% Magnesium, as slowly solidified. S, prismatic, grey, associated with rounded masses of aluminium (white, showing coring) and T (darker grey); Mg_2Al_3 , mid-grey, containing specks of precipitated T. Etched with sodium hydroxide followed by nitric acid. $\times 200$.

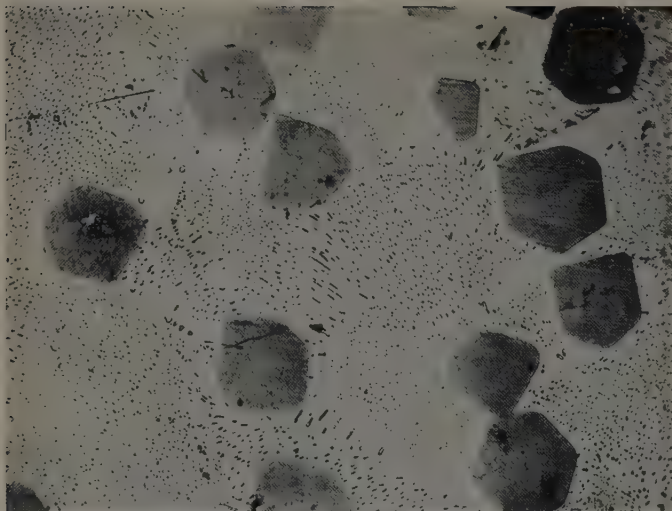


FIG. 10.—Alloy Containing 4% Copper, 33% Magnesium, as slowly solidified. Primary T , dark-grey crystals with regular outline; background, Mg_2Al_3 containing precipitated T in a Widmanstätten structure, and a few globules of aluminium (white, outlined). Etched with sodium hydroxide followed by nitric acid. $\times 200$.



FIG. 11.—Alloy Containing 2% Copper, 33% Magnesium, as slowly solidified. Four crystals of Mg_2Al_3 showing Widmanstätten precipitation of T . Etched with sodium hydroxide followed by nitric acid. $\times 500$.

were extended sufficiently far into this field to permit of isothermals being plotted up to 540° C. The results, converted to atomic percentages, and plotted logarithmically, are shown in Fig. 4.

It will be seen that in the alloys containing higher percentages of copper the slope of the curves is very nearly equal to 1:1, but that the mass-action relationship does not hold when the magnesium content is high. Data for some isothermals of the primary T field have been included in Fig. 4: it is interesting to note that the gradient is very nearly equal to 1:4, thus affording some independent confirmation of the ratio of copper to magnesium atoms in the compound T (Al_6CuMg_4).

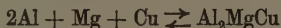
VI.—THE SECONDARY SURFACE.

The surfaces of secondary separation are shown in Fig. 5 (Plate LXII). Each primary field is associated with several secondary fields: the boundaries between the secondary fields have been drawn as thin, full lines, and initial letters have been used to indicate the phases present and their order of separation. The letters A , C , and M have been used, for brevity, to represent the aluminium-rich solid solution, CuAl_2 , and Mg_2Al_3 , respectively.

The isothermals of each secondary field have been drawn as broken lines. In the primary CuAl_2 , S , and T fields the secondary isothermals appear to be straight lines, indicating little change in the homogeneity ranges of these constituents with changing temperature. In the primary aluminium field, however, the secondary isothermals are curved, and the curvature is such as to indicate an increase in the magnesium content of the aluminium-rich solid solution as solidification proceeds: this tendency is more pronounced in the alloys richer in magnesium.

The primary aluminium field, $OJLRUW$, has five associated secondary fields: $BJLD$, in which CuAl_2 is secondary; $DLRG$, in which S is secondary; GRU , in which T is secondary; $HGUW$, in which Mg_2Al_3 is secondary; and finally a small field near the origin, $OBGH$, in which the aluminium-rich solid solution is the only constituent present. The secondary CuAl_2 field can be further sub-divided. Over the greater part of it, that contained within the triangle DKL , solidification is completed at the ternary eutectic of aluminium, CuAl_2 , and S , at a temperature of 507° C. In the remaining portion, represented by the narrow strip $BJKD$, solidification is completed during the separation of the binary eutectic complex Al-CuAl_2 at some temperature above that of the ternary eutectic, and the constituent S does not appear in the micro-sections. The boundary between these two

regions is indicated by a dotted line. The secondary *S* field can also be sub-divided. In the region *DLNE*, the constituents present are aluminium, *S*, and CuAl_2 , and solidification is completed at the ternary-eutectic temperature. Even with slow cooling, CuAl_2 persists slightly to the magnesium side of the line joining the aluminium corner to the point representing the composition of *S*: this suggests that there is a balanced reaction in the liquid phase:



requiring an excess of magnesium for its completion. The structure of an alloy in this field is shown in Fig. 6, Plate LXIII. The primary aluminium crystals show definite evidence of coring: *S*, separating as a binary complex with aluminium, appears in relatively large crystals in half-tone, while the CuAl_2 of the ternary eutectic appears as small dark crystals associated with similar grey crystals of *S*.

In the next region, that contained within the strip *ENPF* (bounded by dotted lines), the alloys are two-phase, consisting of aluminium and *S* only. It is interesting to note that the two-phase field widens as the copper content is reduced. In this region the temperature of separation of the Al-*S* binary complex reaches its maximum value of 518° C. Had the system Al-*S* been truly quasi-binary, this maximum would have been coincident with the quasi-binary line, and at all points along this line solidification would have been completed with the binary separation at 518° C. Under the conditions of cooling employed, the maximum lies on the magnesium side of the quasi-binary line: the excess of magnesium over that required to form Al_2CuMg (*S*) dissolves in the aluminium, which therefore freezes over a range of temperatures, and solidification is completed some degrees below the quasi-binary eutectic temperature.

The structure of an alloy in this region is shown in Fig. 7, Plate LXIII. The coring of the aluminium primary crystals is not very pronounced, and two constituents, aluminium and *S*, are to be seen in the eutectic areas. It can just be seen that the eutectic areas are separated from the primary crystals by a complete shell of the constituent *S*, almost certainly owing to the effects of under-cooling.

On the magnesium side of the two-phase region (*AS*) lies a field *FPQG*, in which the constituent *T* is present. During the separation of the Al-*S* eutectic complex, the composition of the portion of the alloy still liquid follows the binary valley *PQRU*. Any liquid remaining when the composition has reached *R* and the temperature has fallen to 467° C. will react peritectically with the solid *S* to form *T*. Under the conditions of cooling employed, the reaction does not pro-

ceed very far, and stops almost as soon as the S crystals have become surrounded by a sheath of T . Solidification is then completed at some point along the Al- T binary valley, RU . In alloys in the next field, GQR , liquid still persists until the temperature has fallen as low as 451°C ., when the separation of the ternary eutectic Al- T - Mg_2Al_3 takes place. In this field, four phases are present, aluminium, residual S , T , and Mg_2Al_3 . A typical micrograph of an alloy in this field is shown in Fig. 8, Plate LXIV. S occurs as pale-grey nodules enveloped in the rather darker T , while Mg_2Al_3 can be seen outlined but white, and showing faint specks of T precipitated from solid solution.

In the next field, GRU , the binary separation is no longer S but T : the alloys consist of the three phases aluminium, T , and Mg_2Al_3 , and solidification is completed with the separation of the ternary eutectic.

The field $GUWH$, in which Mg_2Al_3 is secondary, is sub-divided into two parts: there is a narrow strip $GVWH$ adjacent to the aluminium-magnesium axis in which all the copper is dissolved either in the aluminium or in the Mg_2Al_3 , and a triangular area GUV in which the copper content exceeds the amount that can be retained in solid solution, and in which therefore the constituent T is present.

Fig. 12 shows, on a larger scale, the constituents present in aluminium-rich alloys as slowly solidified.

The line BD , representing the lower limit of occurrence of CuAl_2 , lies at approximately 0.20–0.25% copper, while the line DEF , corresponding with the first appearance of S , runs almost parallel to the aluminium-magnesium axis and at a distance from it corresponding to about 0.2% copper. The line GH , representing the first appearance of Mg_2Al_3 , lies at about 4.25% magnesium; T first appears, along FG , at rather less than 0.20% copper.

Structures in the primary CuAl_2 field ($JXZL$), Fig. 5 (Plate LXII), do not require detailed comment; as far as it was possible to determine, the secondary isothermals are straight lines running towards the point representing the lower homogeneity limit of CuAl_2 , and are thus consistent with the view that CuAl_2 has only an extremely small capacity for dissolving magnesium.

In the primary S field the secondary isothermals appear to be straight lines running to the composition of S , and all are consistent with the view that the homogeneity range of S is small. The subdivision of the primary field into regions in which CuAl_2 , aluminium, and T are secondary will be clear from Fig. 5.

The structure of an alloy in the $SATM$ field of Fig. 5 is shown in Fig. 9, Plate LXIV. It is somewhat complex. A crystal of primary S (grey) runs diagonally across the field and is in intimate contact in

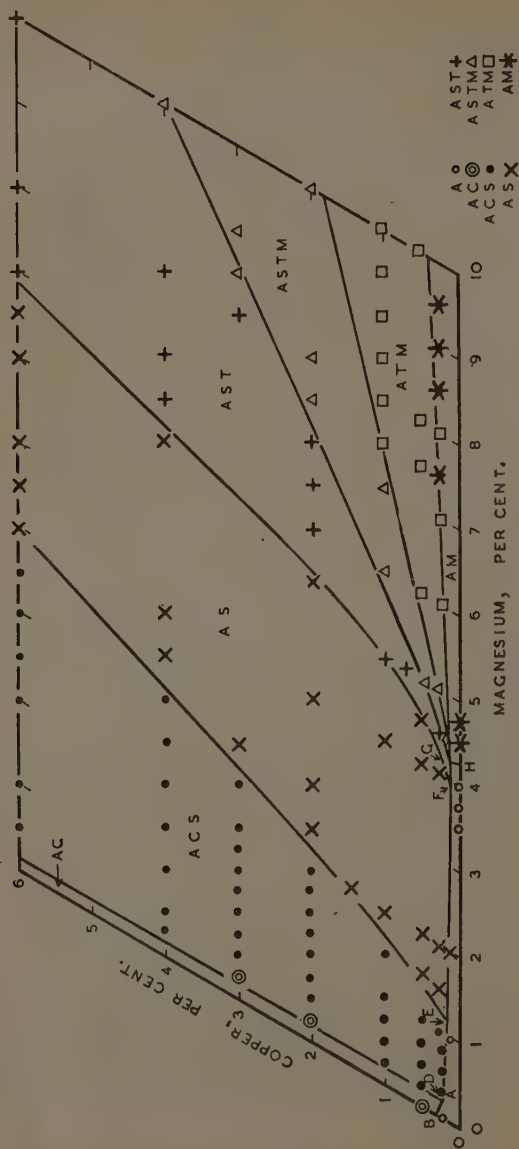


Fig. 12.—Constituents Present : Alloys Slowly Solidified.

two places with rounded masses of secondary aluminium. Elsewhere it is surrounded by a sheath of *T* (dark grey), formed in the peritectic reaction at 467° C. Much of the *T* is associated with aluminium (often heavily cored), the eutectic having a characteristic appearance which may be termed sponge-like. The *T*-Al complex is surrounded by Mg_2Al_3 (rather paler grey), which is the last constituent to solidify, and which is supersaturated with respect to copper at the moment of solidification, depositing the excess below the solidus as a finely dispersed precipitate of *T*.

A dotted line has been inserted in Fig. 5 (Plate LXII), running from the peritectic invariant point *R* to a point, indicated by a six-rayed star, within the homogeneity range of *T*. This line marks the lower limit of the occurrence of *S*. In alloys the compositions of which lie below this line but above the full line running from *R* to some point below the star sign, primary *S* separates, but is completely converted to *T* during the peritectic reaction. Below the full line, *T* is primary. The structure of an alloy in the primary *T* field is shown in Fig. 10, Plate LXV. The primary *T* crystals have a fairly regular outline, and the Widmanstätten precipitation of *T* in the Mg_2Al_3 ground-mass is clearly evident. Aluminium, of the ternary-eutectic generation, can be seen as extremely small white globules in the Mg_2Al_3 . Fig. 11 (Plate LXV) has been included to show the form taken by the precipitated *T* in four Mg_2Al_3 crystals. Detailed examination suggests that the rods of *T* are aligned parallel to the cube axes of the Mg_2Al_3 crystals.

VII.—SECTIONAL DIAGRAMS.

Four vertical sections through the ternary model, showing the constitution, as slowly solidified, of alloy series in which the amount of one of the alloying ingredients is maintained constant, are shown in Figs. 13–16. The letter *L* has been used, for brevity, to indicate the presence of liquid. It was not found possible to determine experimentally the portion of the solidus over the $\text{Al} + S$ field: quenching experiments gave inconsistent results, because constituents just melted tended to re-solidify without change of crystal size or habit. This portion of the solidus has therefore been inserted as a dotted line, reaching a maximum at the same composition as the maximum on the line of secondary arrests but some 5° C. below it.

It is interesting to compare Fig. 13, representing the 5% copper series as slowly solidified, with Fig. 17, which represents the same series under conditions of equilibrium. The latter diagram has been constructed from the isothermal sections given in the papers of Hume-

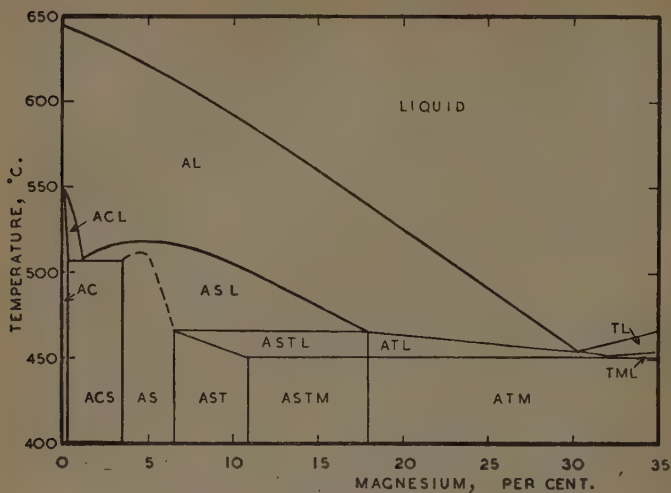


FIG. 13.—Alloys Containing 5% Copper, as slowly solidified.

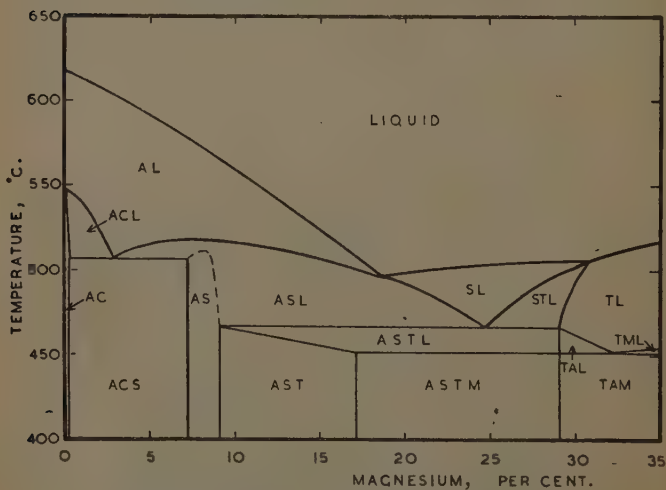


FIG. 14.—Alloys Containing 15% Copper, as slowly solidified.

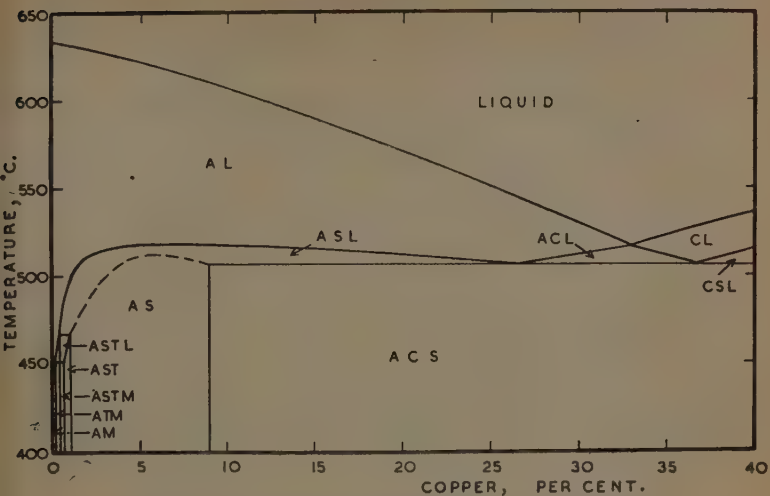


FIG. 15.—Alloys Containing 5% Magnesium, as slowly solidified.

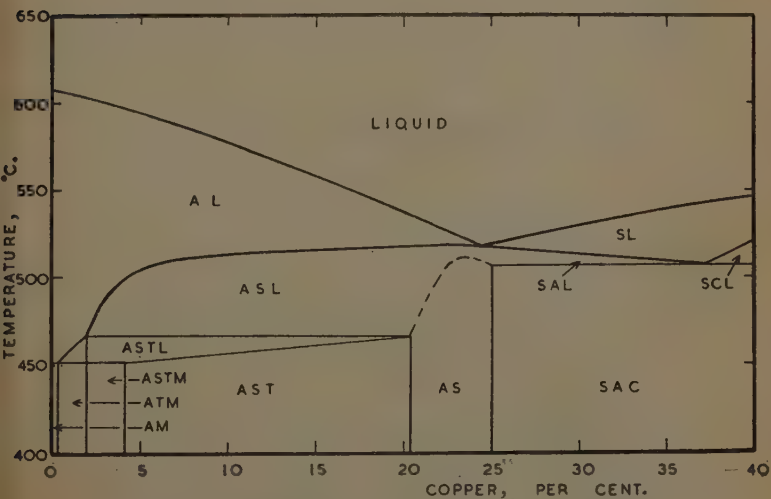


FIG. 16.—Alloys Containing 10% Magnesium, as slowly solidified.

Rothery, Petrov, and their respective colleagues. The four-phase fields have disappeared; the two-phase fields are wider and have sloping boundaries; and a new two-phase field, $\text{Al} + T$, appears.

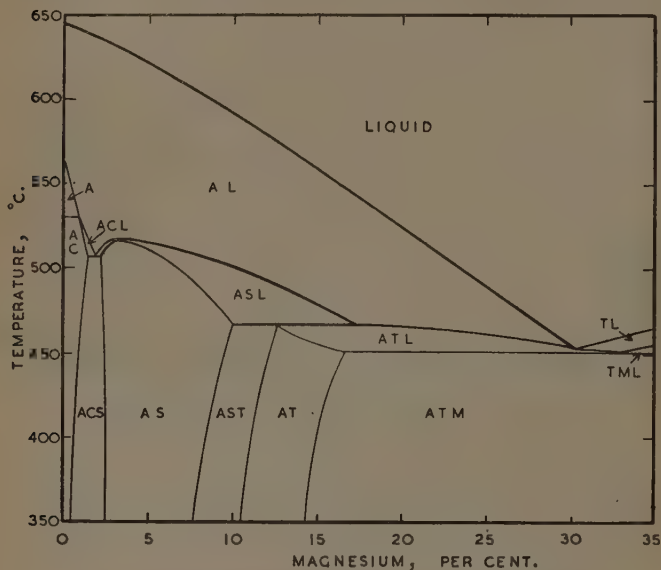


FIG. 17.—Alloys Containing 5% Copper (equilibrium conditions).

VIII.—THE 430° C. ISOTHERMAL.

Work on equilibrium structures below the solidus was limited to an attempt to obtain independent evidence on three points on which the findings of previous investigators are discordant or incomplete.

Little, Hume-Rothery, and Raynor¹⁹ placed the aluminium apex of the three-phase triangle Al-S-CuAl_2 on the equi-atomic line, whereas Petrov and Berg²¹ placed it much nearer to the aluminium-copper axis. Kuznetsov and Guseva¹⁵ placed the aluminium apices of the three-phase triangles Al-S-T and $\text{Al-T-Mg}_2\text{Al}_3$ at the same distance from the aluminium-magnesium axis, at about 0.6% copper, whereas according to Petrov and Berg²¹ the distance is of the order of 0.2% copper, a figure which is consistent with Hume-Rothery's diagrams. Data on the solid solubility of copper in Mg_2Al_3 are reported only by

Petrov and Berg,²¹ whose diagrams suggest a maximum of about 1% at the eutectic temperature.

To investigate the first point of difference, series of alloys were prepared containing 2.0 and 3.5% copper, with magnesium increasing in steps of 0.25% from 0 to 1.5%. Samples were annealed for 14 days at 430° C., and examined microscopically: the results confirmed unequivocally those published by Hume-Rothery and his colleagues. The apex of the Al-CuAl₂-S field was placed at 2.2% Cu, 1.0% Mg.

To determine the position of the apices of the Al-S-T and Al-T-Mg₂Al₃ fields, series of alloys were prepared containing 0.25, 0.5, and 1.0% copper, with magnesium varying from 7.5-20%, and annealed for 14 days at 430° C. It was found that both apices lay close to the aluminium boundary, in both cases between 0 and 0.25% copper. To determine the composition more accurately, counts were made of the number of S and T particles visible on the area of a quarter plate at a fixed magnification: the particles were fairly consistent in size and so it seemed legitimate to extrapolate to zero to obtain the true position of the boundary. The figures thus obtained were:

Al-S-T apex: 0.23% Cu; 9.2% Mg.

Al-T-Mg₂Al₃ apex: 0.16% Cu; 10.2% Mg.

It is impossible to say, from these few observations, whether the Al-T solubility curve follows the mass-action law $[Cu] \times [Mg]^4 = \text{constant}$. It is, however, interesting to note that the values of the solubility products for the two apices, which are, of course, the end-points of the curve in question, work out at 1.060×10^3 and 1.113×10^3 respectively, values which are not inconsistent with the view that the mass-action law holds.

Finally, a study was made of the solubility of copper in Mg₂Al₃. Series of alloys were prepared, containing 20 and 33% magnesium, with copper increasing in steps of 0.25% from 0 to 4%. The solid solubility, at 430° C., appeared to be of the order of 2.5% copper, and from the development of the Widmanstätten structure at lower temperatures, it seemed likely that the solid solubility at 200° C. would not exceed 0.25%, but the figure was not accurately determined. The 430° C. isothermal is shown in Fig. 18.

IX.—THE CONSTITUTION OF COMMERCIAL ALLOYS.

Commercial aluminium alloys containing copper and magnesium usually contain other alloying elements as well, and these exert a profound influence on the structure. Nevertheless, it is important to

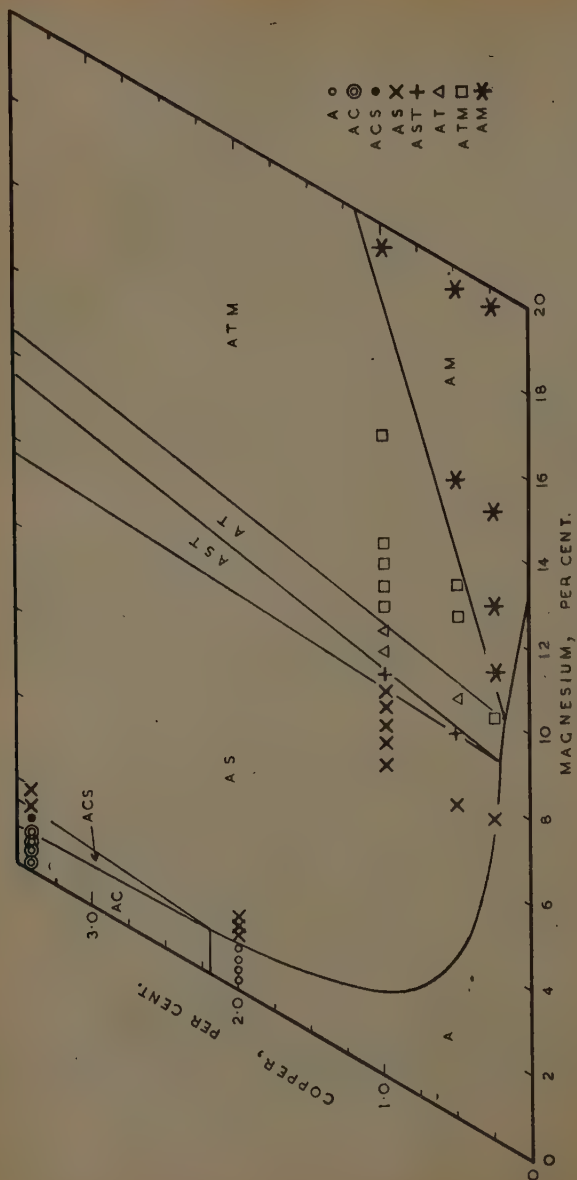


FIG. 18.—The 430° C. Isothermal.

know the constitution of the ternary alloys over the specified range of composition, both under conditions of equilibrium and in the state in which the alloys are initially fabricated.

Ternary alloys containing about 4% copper, with magnesium 0.5–0.8%, may be taken as the basis of that extensive range of heat-treatable alloys of which Duralumin was the first to be developed. Such alloys, as cast, will contain the intermetallic constituents CuAl_2 and S , and their solidus temperature will be that of the ternary eutectic, 507°C . On heat-treating at 500°C . until equilibrium is reached, the alloys will consist entirely of aluminium and CuAl_2 , and the solidus temperature will lie at about $530^\circ\text{--}540^\circ \text{C}$. The solid solution becomes supersaturated on cooling, and under conditions of equilibrium would commence depositing particles of S on passing through the temperature range $350^\circ\text{--}400^\circ \text{C}$. Precipitation of CuAl_2 would also occur.

An alloy containing copper 4, magnesium 1.5% may be taken as the ternary basis of Y alloy, which, in addition, contains 2% nickel. The ternary alloy falls in the $\text{Al-CuAl}_2\text{-}S$ field as cast, and lies just at the aluminium apex of this field on annealing to equilibrium at 500°C . The solidus, in both conditions, is therefore 507°C .

Binary alloys containing from 2–10% magnesium may contain copper as a contaminant. Provided that the extent of this contamination does not exceed 0.1%, the alloys as cast will consist of the aluminium-rich solid solution, plus Mg_2Al_3 if the magnesium content exceeds 4.25%. On annealing, the whole of the magnesium will be taken into solid solution, and will tend to be re-precipitated on cooling. Table V gives the solidus temperatures as cast and under conditions of equilibrium, together with the temperatures at which the solid solution becomes supersaturated on cooling.

TABLE V.—*Thermal Data for Some Binary Aluminium-Magnesium Alloys.*

Composition, % Mg	2	5	10
Solidus, as cast, $^\circ \text{C}$	560	451	451
Solidus, equilibrium, $^\circ \text{C}$	635	595	520
Saturation limit, $^\circ \text{C}$	160	260	390

With copper contamination of the order of 0.1–0.2%, the T constituent will occur, either as eutectic or in the form of precipitate. Such contamination would be without effect on either the liquidus or the solidus temperature. The very great similarity in crystal habit and etching behaviour of T and Mg_2Al_3 containing dissolved copper suggests that crossing the phase boundary between the $\text{Al} + \text{Mg}_2\text{Al}_3$

and $\text{Al} + \text{Mg}_2\text{Al}_3 + T$ fields is unlikely to have much practical significance.

X.—SUMMARY.

Although several papers have been published on the constitution of ternary alloys of aluminium with copper and magnesium under conditions of equilibrium, little has hitherto been known about their constitution under the conditions of metastable equilibrium likely to be met with in industrial practice, and it is with this that the present investigation is chiefly concerned.

A re-determination of the liquidus surface over the greater part of the range 0–40% copper, 0–35% magnesium has confirmed the occurrence of the binary constituents CuAl_2 and Mg_2Al_3 and of two ternary bodies $S(\text{Al}_2\text{CuMg})$ and $T(\text{Al}_6\text{CuMg}_4)$, and has led to co-ordinates of the ternary invariant points in reasonably close agreement with those published by Japanese and Russian investigators. It has been confirmed that in alloys containing a preponderance of copper over magnesium there is a ternary eutectic of Al , CuAl_2 , and S , containing 33.0% Cu , 6.1% Mg and freezing at 507°C . In alloys containing a preponderance of magnesium, S is converted peritectically to T , the invariant point $\text{Al}-S-T$ -liquid lying at 26.0% Mg , 10% Cu , 467°C . Aluminium forms a ternary eutectic with T and Mg_2Al_3 , the composition being 2.7% Cu , 32.0% Mg and the temperature 451°C . The dividing line between the two partial systems is that along which copper and magnesium are approximately in equi-atomic proportions, or 2.6 : 1 by weight. Here the binary valley between the aluminium and S fields reaches its highest temperature, 518°C . The $\text{Al}-S$ system appears to be truly quasi-binary only under conditions of equilibrium : in the alloys as slowly solidified a small excess of magnesium over that necessary to form Al_2CuMg is required in order to ensure complete suppression of CuAl_2 , suggesting the existence of a balanced reaction in the liquid. The excess magnesium is taken into solution by the aluminium, which therefore freezes over a range of temperatures, and not at the equilibrium temperature of 518°C . The peritectic reaction between liquid and S to form T rarely proceeds to completion during solidification, and usually ceases when the S crystals have become enveloped in a sheath of T , giving rise to duplex crystals in the micro-sections. The liquidus temperatures in the primary aluminium field fall rapidly with increasing magnesium content, and relatively slowly with increasing copper. In the primary S and T fields, the isothermals follow fairly closely the respective mass-action laws $[\text{Cu}] \times [\text{Mg}] = \text{constant}$ and $[\text{Cu}] \times [\text{Mg}]^4 = \text{constant}$.

The isothermals of the secondary surfaces associated with the primary aluminium field are curved, suggesting that the magnesium content of the aluminium-rich solid solution increases as solidification proceeds. In the remaining primary fields, the secondary isothermals are straight, and their directions are consistent with small homogeneity ranges, little affected by temperature, of the constituents separating.

In the alloys as slowly solidified, the solubility of copper and magnesium in solid aluminium is relatively small, CuAl_2 appearing in the micro-sections when the copper content exceeds about 0.25%, S when the copper exceeds 0.25% and the magnesium content 0.20%, T when the copper content exceeds about 0.2% and the magnesium 4.2%, and Mg_2Al_3 when the magnesium content exceeds 4.25%. Under these conditions, Mg_2Al_3 appears to be capable of dissolving about 1.6% copper at the eutectic temperature, but much of this is rejected on cooling, giving rise to a well developed Widmanstätten precipitation of T . Thus the ternary alloys which may be regarded as the basis of the heat-treatable commercial alloys containing about copper 4, magnesium 0.5%, with manganese and silicon to about 0.5%, all lie in the $\text{Al-CuAl}_2\text{-S}$ field, and their solidus temperature is that of the ternary eutectic, 507° C.

Work on equilibrium structure below the solidus has been confined to obtaining independent evidence on points on which earlier investigations are not concordant. It has been found that at 430° C. the apex of the three-phase field $\text{Al-CuAl}_2\text{-S}$ lies at approximately 2.2% Cu, 1.0% Mg, and is therefore close to the equi-atomic line, in accordance with the findings of Hume-Rothery and his colleagues. The coordinates of the apices of the Al-S-T and $\text{Al-T-Mg}_2\text{Al}_3$ fields have been placed at 0.23% Cu, 9.2% Mg and 0.16% Cu, 10.2% Mg respectively, figures which agree reasonably well with those reported by Petrov and his colleagues. It was found that the equilibrium solubility of copper in Mg_2Al_3 at 430° C. was of the order of 2.5%, a figure rather higher than that found by Petrov.

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RELATION BETWEEN THE DEGREE OF ORDER AND THE LATTICE PARAMETER OF Cu_3Au .*

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SYNOPSIS.

The lattice parameter of the alloy Cu_3Au was measured with the alloy in different degrees of short-distance order obtained by quenching from temperatures both above and below the critical temperature. The parameter is approximately linearly related to the degree of order. It is suggested, as a consequence, that the lattice parameters of solid solutions are better correlated with interatomic bond lengths than with atomic diameters, although the bond lengths may vary with change in electron concentration in the alloys. The parameters of the binary solid solutions between the elements copper, silver, and gold are examined in the light of this suggestion, and the bond lengths correlated with the character of the constitutional diagrams.

I.—INTRODUCTION.

THE alloy Cu_3Au has been studied widely in view of the ease with which the order-disorder transformation can be arrested at varying degrees by quenching from various temperatures. X-ray examination of this alloy formed one of the first studies of superlattice formation and, although a marked reduction of lattice parameter on ordering was observed, it is surprising that a careful examination of the variation of parameter with change in degree of order does not appear to have been made. Jones and Sykes¹ showed that a considerable variation in lattice parameter occurred with variation in the conditions of treatment of the alloy and, using a constant annealing temperature to give a fixed degree of order, related the parameter to the size of the anti-phase nuclei. The explanation put forward was that the nuclei were surrounded by films of disordered material and that the observed lattice parameter was directly proportional to the relative amounts of ordered and disordered material present. The true parameter of the ordered material can only be obtained if the nuclei are allowed to grow to a size comparable to the grain-size of the alloy, so that the disordered films form a small proportion of the whole. A complete exploration of the dependence of the parameter on the degree of order was not made by these workers.

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The investigation to be described was therefore undertaken to determine this relationship with particular regard to samples which, by annealing at temperatures above the critical ordering temperature and quenching, are caused to have only a low degree of short-distance order, but, because of the absence of long-distance order, give no superlattice lines in a diffraction photograph. Since this work was carried out Owen and Sim ² have reported the results of a similar investigation of the effect of time of annealing below the critical ordering temperature on the lattice parameter and used the results in a discussion of the growth and size of nuclei; and Owen and Liu ³ have measured the lattice parameter at various temperatures between room temperature and 620° C. In the latter work, while the change in parameter with change in degree of order influences the results, and the sudden change at the critical temperature is very clear, the smaller changes both above and below the critical temperature are superimposed on the normal thermal expansion and are not readily separated. Nevertheless, the observation of abnormally high expansion coefficients in the region of the critical temperature indicates that the parameter increases with reduction of short-distance order.

II.—MATERIAL AND HEAT-TREATMENT.

The material used was supplied by Messrs. Johnson, Matthey and Company, Limited, in the form of 0.4 mm. dia. wire. It had been initially drawn to 1 mm. dia., then vacuum-annealed at 950° C. for 4 hr. to remove coring, lightly abraded to remove the surface layers, and finally drawn to the required diameter. The composition was given by the suppliers as 24.09 at.-% gold and a check analysis gave 24.35 at.-%. A portion of the wire was rolled to ribbon about 0.06 mm. thick and 1.5 mm. wide and cut into lengths of about 5 mm., four of which were subjected to each treatment and used for the accurate parameter measurements. A length of about 1 cm. of the wire was also included in each treatment and a Debye-Scherrer photograph taken to record the onset of long-distance order by the appearance of the superlattice lines.

The samples for each heat-treatment were enclosed in thin Pyrex-glass tubes, evacuated and sealed, and they were all recrystallized to obtain a uniform grain-size by heating to 650° C. for 30 min., and then air-cooled. The tubes containing the samples for temperatures above the critical point were then heated individually in a small tube furnace to temperatures in the range 400°–600° C., for periods varying between 6 hr. and 1 hr., the longer periods being given at the lower temperatures

to ensure that equilibrium was obtained; rapidly withdrawn from the furnace and quenched in cold water. The tubes containing the samples to be heated to temperatures below the critical point were all heated together to a temperature of 370°C . for 90 hr., following the procedure advised by Jones and Sykes for the most rapid attainment of the equilibrium degree of order. At this temperature the anti-phase nuclei grow fairly rapidly until the whole of each grain consists of a single system of ordering. For the work in hand it was essential that this condition should be attained.

At the conclusion of this treatment, one tube was removed from the furnace and rapidly quenched; a powder photograph was taken to confirm that superlattice lines had been introduced and that they were equally as sharp as the normal lines of the diffraction pattern, proving that the anti-phase nuclei had grown satisfactorily. After a further 24 hr. at 370°C . the temperature was dropped to 350°C . over a period of 24 hr. and then maintained at that temperature for 96 hr., after which another tube was removed from the furnace and quenched. Proceeding in this manner and giving about 100 hr. stand at each temperature, samples were obtained which were taken to be representative of the equilibrium conditions at temperatures at 50° intervals down to 200°C .

III.—MEASUREMENT OF LATTICE PARAMETERS.

The parameters of the samples were measured by a back-reflection technique, the traces being recorded on a flat film which was rotated about the incident beam during the course of the exposure. The samples, consisting of the four short lengths of strip, were cemented side by side on to a small piece of film base so as to form an area about 5 mm. square, and this was placed at a distance of about 10 cm. from the film and also rotated about the axis of the incident beam. The distance from film to sample was kept nominally constant and any fortuitous variation in this quantity, as well as any shrinkage in the film, was taken care of by a method of extrapolation to be described shortly. The $K\alpha$ radiation of nickel was used, and this gives suitable reflections from the (420) planes at about 82° and from the (331) planes at about 75° . The parameter values derived from the measurement of these two sets of reflections enabled the true value to be obtained by plotting against the function $\cos 2\theta(1 + \cos 2\theta)$ and extrapolating to zero, i.e. $\theta = 90^\circ$. This function has a linear relationship with the calculated parameter for a given uncertainty in the specimen-to-film distance or in the amount of film shrinkage.

In Fig. 1 let the specimen-to-film distance be D and the distance of

the diffracted line from the centre of the film be x . Then from $\sin 2\theta = x/\sqrt{(x^2 + D^2)}$ we have:

$$\frac{d\theta}{dD} = - \frac{\cos^2 2\theta \cdot \tan 2\theta}{2D} \quad \dots \quad (1)$$

and from $\sin \theta = \lambda/2d$ we have:

$$\frac{dd}{d\theta} = - (2d^2 \cos \theta)/\lambda \quad \dots \quad (2)$$

Combining (1) and (2) and substituting $2 \sin \theta$ for λ/d , this reduces to:

$$2 \frac{dd}{d} = \cos 2\theta (1 + \cos 2\theta) \frac{dD}{D}.$$

That is to say that a given proportionate error in the specimen-to-film distance produces a proportionate error in plane spacing, or in lattice parameter, directly proportional to $\cos 2\theta(1 + \cos 2\theta)$. If a variation in the distance x occurs owing to film shrinkage, since for a constant value of θ :

$$\frac{dx}{x} = \frac{dD}{D},$$

the error introduced into the calculated parameter is directly proportional to the same function.

Hence, by plotting the calculated parameter for each set of

TABLE I.—*Lattice Parameters of Copper-Gold Alloy with 24.09 at.-% Gold.*

Sample No.	Final Heat-Treatment.	Lattice Parameter at 20° C., in kX.
1	1 hr. at 600° C.	3.7432 ₇
2	1 hr. at 550° C.	3.7431 ₆
3	2 hr. at 500° C.	3.7431 ₄
4	4 hr. at 450° C.	3.7429 ₀
5	5 hr. at 425° C.	3.7429 ₀
6	6 hr. at 400° C.	3.7426 ₀
7	90 hr. at 370° C.	3.7383 ₄
8	114 hr. at 370° + 96 hr. at 350° C.	3.7380 ₈
9	As Sample 8 + 96 hr. at 300° C.	3.7372 ₇
10	As Sample 9 + 96 hr. at 250° C.	3.7368 ₁
11	As Sample 10 + 112 hr. at 200° C.	3.7366 ₇

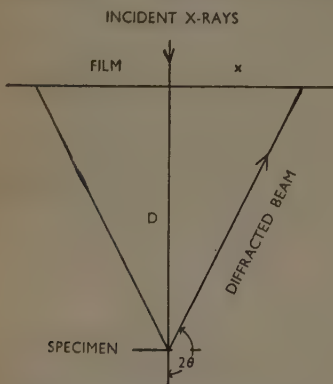


FIG. 1.—Arrangement of Specimen and Film for Parameter Measurements.

diffracted lines against this function and extrapolating to zero, the true parameter is obtained.

In general, three photographs of each sample were taken, and an analysis of the results showed that, after correcting to 20°C. , the standard deviation from the mean value was 0.00005 kX. The parameter values quoted have been corrected for refraction, and the wave-lengths used were Siegbahn's.

The details of heat-treatment and the mean parameter for each sample are recorded in Table I.

IV.—DISCUSSION OF RESULTS.

The relationship between temperature and degree of short-distance order as defined by Bethe⁴ has been calculated for a face-centred cubic

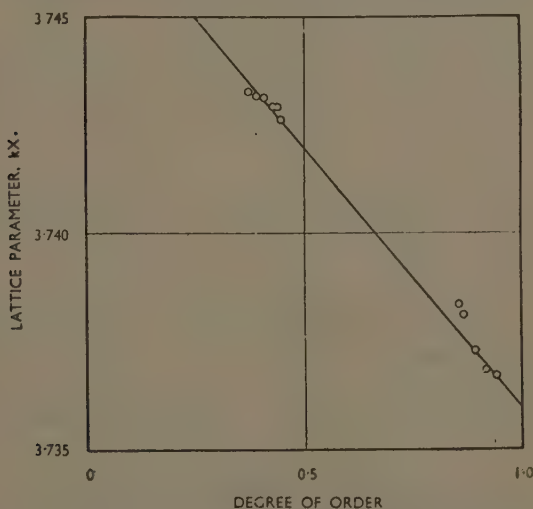


FIG. 2.—Lattice Parameter of Cu_3Au Plotted Against Degree of Short-Distance Order.

lattice of the formula A_3B by Peierls,⁵ and the observed lattice parameters are plotted against the values of σ given by his theory in Fig. 2. It is seen that, within the accuracy of the observations, all the points fall on a straight line with the exception of those corresponding to temperatures just below the critical ordering temperature.

In Fig. 3 the observed parameters are plotted against the tempera-

ture of final annealing, and the curve derived from Peierls's theory by using the straight line of Fig. 2 to convert degree of order to parameter, is also included. This Figure indicates that, while at temperatures

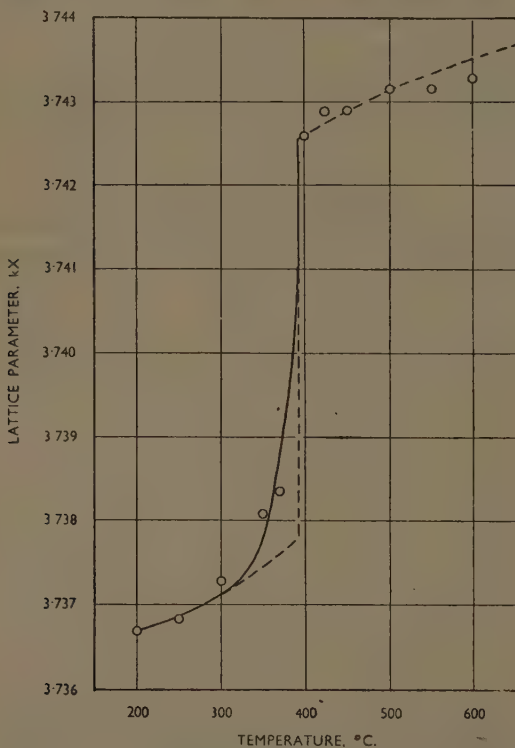


FIG. 3.—Lattice Parameter of Cu_3Au Plotted Against Annealing Temperature.

KEY.

- Observed values.
- Calculated from Peierls's theory.
- Calculated from Sykes and Jones's specific-heat measurements.

above the critical the agreement between the observed parameters and the curve derived from the theory is good, at temperatures immediately below the critical the parameter measurements suggest a more rapid change in degree of order than that predicted by the theory. This is

in agreement with the findings of Sykes and Jones ⁶ from specific-heat measurements; the continuous curve in Fig. 3 has been plotted from the results of these workers, the observed energy changes (which are a measure of the change in degree of order) being converted to lattice parameters by using the conditions at 200° and 400° C. as fixed points. Good agreement between this curve and the measured lattice parameters is apparent.

From the straight line plot of Fig. 2 the parameters of an alloy in the fully ordered state ($\sigma = 1$) and in the completely disordered state ($\sigma = 0$) can be derived, and these are respectively 3.7359 kX. and 3.7478 kX. Correcting for the deviation in composition of the sample from that of Cu_3Au , by the parameter-composition curve of Johansson and Linde,⁷ the values become 3.7409 kX. and 3.7528 kX. respectively.

V.—THEORETICAL CONSIDERATIONS.

In considering the lattice parameters of binary solid solutions it is usual to regard the atoms as spheres, the radii of which, to a first approximation, remain constant. The lattice parameter of an alloy is then related to the mean atomic radius r_0 which is given by :

$$r_0 = \Sigma pr$$

where p is the atomic fraction of the element of atomic radius r . This is the well-known Vegard's law. Most alloy systems deviate from this law to a greater or less extent, and the deviations are frequently regarded as due to a change in the effective atomic radius of one or both of the constituents with change in composition of the alloy. The above expression does not, however, allow for the change in lattice parameter on ordering. If, on the other hand, the lattice parameter is regarded as being related to the mean interatomic bond length a different situation arises, for deviations from the straight-line law can occur without the lengths of the three possible bonds varying with composition of the alloy, while parameter changes on ordering are a consequence of the variation in proportions of the different bonds.

In a binary alloy of metals A and B , containing an atomic fraction p of B , the three types of bond will occur in the following proportions if the atoms are randomly distributed among the lattice sites :

$$\begin{array}{ll} AA & (1-p)^2 \\ BB & p^2 \\ AB & 2p(1-p) \end{array}$$

and the mean bond length will be :

$$d_0 = (1-p)^2 d_{AA} + p^2 d_{BB} + 2p(1-p) d_{AB} \quad . \quad . \quad (3)$$

For the alloy A_3B under consideration this gives:

$$d_r = 0.5625\bar{d}_{AA} + 0.0625\bar{d}_{BB} + 0.375\bar{d}_{AB} \quad . \quad . \quad . \quad (4)$$

In the fully ordered state of the face-centred cubic lattice the distribution of bonds is modified so that the A atoms, a fraction 0.75 of the whole, each have 8 A atoms and 4 B atoms as nearest neighbours; while the fraction 0.25 of B atoms each have 12 A atoms as neighbours. Hence the mean bond length is given by:

$$d_s = 0.5\bar{d}_{AA} + 0.5\bar{d}_{AB} \quad . \quad . \quad . \quad . \quad (5)$$

In the intermediate state, with degree of order σ , the mean bond length becomes:

$$d_\sigma = \frac{1}{8}(3 + \sigma)\bar{d}_{AB} + \frac{1}{16}(9 - \sigma)\bar{d}_{AA} + \frac{1}{16}(1 - \sigma)\bar{d}_{BB} \quad . \quad (6)$$

Thus, assuming that the parameter is proportional to the mean bond length, we get a linear relationship between parameter and degree of order, as is observed.

If the various bond lengths remained constant throughout the whole range of composition of an alloy system, equation (3) would lead to the conclusion that the deviation from Vegard's law would be positive or negative according as \bar{d}_{AB} is greater or less than $\frac{1}{2}(\bar{d}_{AA} + \bar{d}_{BB})$; while the change in parameter on ordering would be in the same direction since AB bonds are then substituted for AA and BB bonds. In the copper-gold system, which shows a positive deviation from Vegard's law but a reduction in the parameter with increase in degree of order, it must be concluded that the bond lengths vary with composition. Further proof of this is obtained if the interatomic distances in the pure metals and the values of d_r and d_s derived from the previously quoted parameters for $\sigma = 0$ and $\sigma = 1$ are put into equations (4) and (5); the values of \bar{d}_{AB} which are then obtained are not the same from the two equations. It is therefore clear that, in general, the various bond lengths cannot be regarded as constant throughout a series of alloys, so that, whereas a change of parameter on ordering is explained by the change in the proportions of the different types of bond, deviations from Vegard's law may necessitate also a variation in the bond lengths with changing composition. The situation is thus reached in which, in order to explain the variation in lattice parameter in a simple binary alloy system, the relationship between each of the three bond lengths and the composition of the alloy is required.

There is some evidence from the work of Owen and his collaborators⁸ that the bond lengths might be linearly related to the electron concentration. It was shown that the changes of the lattice parameters of copper, silver, and gold produced by small additions of the elements from copper to arsenic in the first long period, and of the elements from

silver to antimony in the second long period, are approximately proportional to the valency of the solute metal. Although the atomic size of the pure solutes changes progressively with increasing valency, these changes are much less regular than the changes in the parameters of the solid solutions produced by equi-atomic additions of the solutes. If this supposition were true, it would be necessary to determine six variables, two for each type of bond, before the parameter of any alloy could be calculated. Unfortunately, there are insufficient data available to enable these values to be determined. In the case of pure metals with simple structures the bond lengths of these are immediately available, but in an alloy system which forms no superlattice only one equation can be derived from the parameter-composition curve to cover the four remaining variables. The parameter change accompanying a disorder-order change of the Cu_3Au type gives one more equation, while the formation of a superlattice involving a structure with two parameters, such as the tetragonal lattice of CuAu , provides two equations; but these equations are not all independent, and in no system has it been found possible to obtain sufficient equations unequivocally to derive the full details of the variations in the bond lengths. Nevertheless, it is of interest to consider the parameter variations of some simple alloy systems with the suggested theory in mind.

1. Copper-Silver.

Since these two metals have the same valency and there is little doubt that they are ionized to the same degree in the solid state, it is reasonable to consider that the constant electron : atom ratio will lead to constant values of the bond lengths throughout the system. The solid solubility is limited at each end and it is most convenient to derive the length of the bond between unlike atoms from the terminal slopes of the parameter-composition curves. By differentiating equation (3) and putting $p = 0$ we obtain :

$$\frac{dd_0}{dp} = \frac{dd_{AA}}{dp} + 2(d_{AB} - d_{AA}) \quad . \quad . \quad . \quad (7)$$

Since in this system d_{AA} is considered to remain constant, the initial slope of the curve is given by $2(d_{AB} - d_{AA})$. Similarly, the final slope of the curve at the point $p = 1$ is given by $2(d_{BB} - d_{AB})$. Taking the values of change of parameter with composition quoted by Owen⁸ and d_{AA} and d_{BB} from the parameters of the pure metals, we get in the copper-rich alloys $d_{AB} = 2.7489$ kX. and in the silver-rich alloys $d_{AB} = 2.7491$ kX. The agreement between these two values is very good and

confirms that the observed parameters can be explained with the three bond lengths constant throughout the system. Furthermore, since the bond length between the unlike atoms is greater than the mean of the two bond lengths for pairs of like metals (2.7172 kX.), it means that the bonds between the unlike atoms represent a higher state of energy than the bonds between the like atoms. The fact that alloys within a wide range of composition in this system separate into two phases based on the two pure metals is in conformity with this interpretation.

2. *Silver-Gold.*

It has been shown by Sachs and Weerts⁹ that the mean interatomic distance of an alloy of this system can be expressed by the equation :

$$\bar{d}_0 = (1 - p)d_{Au} + pd_{Ag} - 0.0170p(1 - p)$$

This conforms to equation (3) if $\bar{d}_{AA} + \bar{d}_{BB} - 2\bar{d}_{AB}$ is made equal to 0.0170 kX. The parameters of these alloys can therefore be explained if the bond lengths are taken to be independent of composition, with the bond between unlike atoms only slightly less than the mean of the bonds between like atoms. This could be taken as conforming with the observation that, while on the one hand the alloys consist of an unbroken series of solid solutions, there being no tendency for the like atoms to associate together at the expense of bonds between the unlike atoms, on the other hand the relatively slight tendency of the unlike atoms to move together is insufficient to lead to the formation of a superlattice.

3. *Copper-Gold.*

Since the parameter-composition curve of these alloys shows a positive deviation from Vegard's law, while the ordered alloys have a smaller parameter than the disordered alloys, it is concluded that the parameter variations can only be explained by the individual bond lengths varying with the composition of the alloy. Following the conception that the bond lengths are related to the electron : atom ratio, this leads to the conclusion that copper and gold have different effective valencies in the solid state. Raynor¹⁰ has suggested that gold may have an effective valency greater than 1 when alloyed with certain elements which deform the gold ion, but copper was not included among these.

The alloy Cu_3Au has been dealt with experimentally above, but there is some interest in considering the alloy $CuAu$, for the tetragonal structure of the superlattice allows the bond length between unlike atoms to

be compared with the mean of the bond lengths between like atoms. In the fully ordered state all the bonds in the [101] directions of the lattice are between unlike atoms, so the lattice parameters give :

$$d_{AB} = \frac{1}{2}\sqrt{(a_0^2 + c_0^2)}$$

The bonds in the [110] directions consist of equal proportions of Cu-Cu and Au-Au bonds, so that we obtain :

$$d_{AA} + d_{BB} = a_0\sqrt{2}.$$

Using the parameters given by Hultgren and Tarnopol¹¹ for the highest degree of order they examined and assuming that the alloys were then in the fully ordered condition, we find $\frac{1}{2}(d_{AA} + d_{BB}) = 2.7939$ kX. and $d_{AB} = 2.6997$ kX. The large reduction from the former to the latter is in conformity with the formation of a superlattice.

VI.—CONCLUSIONS.

The observed linear relationship between the lattice parameter of the alloy Cu_3Au and the degree of short-distance order leads to the suggestion that the lattice parameters of solid solutions are better considered as related to the mean bond length than to the mean atomic diameter. It is necessary, however, in order fully to cover the observed deviations from Vegard's law and the parameter changes on ordering, to assume that the bond lengths can vary with composition—possibly linearly with change in free electron concentration—and in no system in which such changes occur has it been found possible to determine the full details of the bond lengths.

In the three binary systems between the elements copper, silver, and gold it is shown that the formation of (a) two phases based on the pure metals, (b) a uniform range of solid solutions with no superlattice, or (c) a superlattice, is dependent on whether the bond length between unlike atoms is (i) greater than, (ii) approximately equal to, or (iii) less than the mean of the bond lengths between like atoms.

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CRYSTALLITE THEORY OF STRENGTH OF 1169 METALS.*

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SYNOPSIS.

Evidence is put forward for the view that the metallic grain contains a fundamental unit of structure below which the grain cannot be broken down by plastic deformation at room temperature. The lower limiting size of the unit, termed "crystallite", has a characteristic value for a given metal. This size has been determined for a group of body-centred cubic metals—iron, molybdenum, tantalum, and tungsten—and, from the measurements, the ultimate tensile strength of these metals has been calculated on the hypothesis that the crystallite sets a limit to the normal mode of deformation by slip. The measurement of the crystallite size has been carried out by X-ray diffraction methods which utilize two recent developments to avoid the complications of internal strains which also affect the X-ray reflections. The limiting crystallite size obtained has the following values: iron 3, molybdenum 4.2, tantalum 2.4, and tungsten 2.9×10^{-6} cm.

I.—INTRODUCTION.

In this paper evidence is put forward for the view that the metallic grain contains an elementary crystalline unit with a size characteristic of the metal, and that the strength of the metal is determined by the size of this unit, for which the term "crystallite" will be used. The crystallite size has been measured for a group of body-centred cubic metals—iron, molybdenum, tantalum, and tungsten—and from the measurements the ultimate strength of the metals has been calculated on the hypothesis that the crystallite sets a limit to the normal mode of deformation by slip. The calculated values agree favourably with the strengths observed.

The measurement of crystallite size utilizes a somewhat specialized X-ray technique, but it is hoped that the matter has been presented in a way which may be of general interest, in view of the bearing on the universal problem of deformation and strength. A summary is first given of previous work on which the present investigation is based. The relevant measurements and their application are then concentrated at the end of the paper.

At the same time the X-ray work described in the intervening Sections may be of interest because it makes use of two developments. Firstly, the observation that the internal strains in systematically

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deformed metals in general are directional, making it possible to avoid complications due to irregular lattice strains which hitherto have rendered the interpretation of the X-ray reflections from deformed metals rather difficult.¹ Secondly, the practicability of obtaining X-ray back-reflection photographs with wave-lengths much shorter than those normally used, and, as a result, of distinguishing the effects of small crystallite size, which vary with the wave-length, from the effects of the irregular lattice strains, which do not.²

II.—PREVIOUS WORK.

The existence of the crystallite and its relation to the deformation and strength of a metal are indicated by the following experimental observations.³

(1) Plastic deformation breaks down the grains into much smaller elements. They can be recognized directly in X-ray diffraction examination because they may exhibit crystallographic orientations which differ widely from that of the parent grain. Experimental proof of the fragmentation is then provided by the angular spread of the X-ray reflections which is to be seen when an initially annealed metal is deformed progressively, a change analogous to the reflection of light from a mirror broken into a mosaic. An illustration is provided by Figs. 4-5 (Plate LXVI), which record the reflection of an X-ray beam from a single grain in a coarse-grained test-piece of aluminium before and after deformation. Before deformation the grain reflects mainly in one direction, but afterwards it reflects over the large angular range corresponding to the spread along the circumference of the ring. Measurement of the spread for different reflection angles and different rings shows that it is in general too large to be explained by elastic bending of the reflecting atomic planes, which also might spread the reflections. Bending is likely to occur to some extent, but it produces relatively second-order effects.

The X-rays cannot indicate the angular tilt of neighbouring crystallites, but only the range summed over the grain or grains covered by the incident beam. The orientation may change from one crystallite to the next by small steps. Also the X-ray results indicate that a grain does not appear to break down by stages to produce two fragments, then four, and so on. The grain tends to dissociate at once to the crystallite formation. The effect of progressive deformation, which in practice is never homogeneous, is to spread the breakdown from point to point rather than to intensify it at one locality, except possibly in fatigue stressing. The details of the breaking down exhibit other features of

interest. It is desired here, however, merely to indicate the evidence for the potential existence of the crystallites in an annealed grain, shown by the extended range of orientations which can be produced by an appropriate mode of plastic deformation.

(2) It has been shown that for metals so far examined the crystallite size lies between an upper limit of 10^{-4} cm. and a lower limit of about 10^{-6} cm., and has a characteristic value for a given metal at room temperature.⁴

The upper limit is set simply by the observation that the X-ray reflection arc or ring from the deformed metal is not a collection of discrete reflection spots, as it is from the annealed metal, but is continuous. The continuity indicates that the number of reflecting elements is so great that the reflection spots coalesce. Consideration of the number of elements in unit volume required to produce coalescence of the reflection spots under the usual experimental conditions, shows that their size cannot be greater than about 10^{-4} cm. The same result is found also from direct experiments on powders of different particle-size. The coalescence would be accentuated by any blurring of the reflection spots which might arise under certain conditions from distortion of the spacing of the reflecting planes, but the same degree of coalescence can be obtained under experimental conditions where the effect of such distortion is negligible, as at small reflection angles. In this way, leaving aside the trivial case of metals which recrystallize during deformation, it has been found that the grains of the various metals tested have exhibited the breakdown to crystallites at least 10^{-4} cm. in size.

The lower limit is set by two considerations. Firstly, diffraction theory shows that the degree of diffusion or radial broadening of an X-ray reflection ring is inversely proportional to the size of the reflecting elements. The broadening in practice is negligible for sizes of 10^{-4} cm. or more, but increases rapidly as the size becomes less than 10^{-4} cm. Secondly, it has been found that as a metal is plastically deformed the broadening sets in quite quickly, but soon reaches a limiting value which is not exceeded however extensive may be any further deformation; also the limiting breadth has a specific value for a particular metal. Therefore it follows from these two considerations that the size of the crystallites produced during deformation of a given metal exhibits a characteristic lower limit. It should be noted that this observation holds even if the broadening were due partly to other factors such as lattice distortions; the effect of such factors, if present, would be merely to complicate measurement of the contribution due to the small crystallite size. The lower limit lies usually between 10^{-5} and 10^{-6} cm.

(3) Finally, study of the crystallite formation and the strength, as a

metal is systematically deformed, has indicated that the two are related and that the maximum strength corresponds to the reduction of the crystallites to the lower limiting size.⁵

This relation, which is the main object of the present work, will be discussed more fully later. It will be noted, however, that if the two are related, a metal will possess an intrinsic maximum strength; although the extent to which it is realized before fracture in a given mode of testing will depend also on other factors. In particular it will depend on the extent to which the breakdown is allowed to permeate in a uniform way throughout a test-piece; a contrast in this respect is provided by a compression test and a fatigue test. Also it will depend on whether the conditions of deformation are favourable for propagation of an incipient crack; a contrast here would be a compression test and an Izod test.

It will be noted also that the strength of a metal will be a more systematic and reproducible property than the strength of other crystalline solids, such as ionic crystals, where the mosaic structure is essentially a haphazard feature. It is to avoid confusion with the indefinite "mosaic element" of other solids that the term "crystallite" has been chosen to signify the fine structure of the metallic grain.

The limiting crystallite size for the metals studied in the present work has been obtained from the broadening of the X-ray diffraction rings, following the particular procedures outlined in the following Sections.

III.—DETERMINATION OF CRYSTALLITE SIZE.

1. *Causes of Broadening of the X-Ray Reflections.*

The radial broadening of the X-ray reflection rings from plastically deformed metals may be very marked. The effect has therefore been the subject of much study, and various causes have been postulated from time to time. Only two have been substantiated by experiment.

One is the factor of sub-microscopic particle size already mentioned. It operates because the small particle contains too few atomic planes for effective resolution of the reflections. Instead of occurring at a precise reflection angle θ , the reflection is spread over a range $\delta\theta$, which is related to the linear particle size l by the formula first given by Scherrer⁶:

$$\beta = \delta\theta = \frac{\lambda}{l} \sec \theta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ is the wave-length of the X-rays.

The second factor is that of irregular lattice strains, which may arise from internal stresses. The reflection angle θ and the spacing d

of a set of lattice planes are related by the Bragg law, $2d \sin \theta = \lambda$. If the spacing changes by amounts up to δd from one reflecting element to another, then the reflection angle will range over the value $\delta \theta$ given by :

$$\delta \theta = - \frac{\delta d}{d} \tan \theta \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The residual strains met with in cold-worked metals in practice are of the type which changes the spacing in the manner described by this relation. This has been shown by the work of Smith and Wood^{7,8} on the lattice stress-strain curve of various metals.

Other factors, which involve more irregular distortion of the lattice, have been suggested. None has been shown to produce effects comparable with the two mentioned above. Indications are, in fact, that such distortions are very localized, as when one metal is alloyed with another, and that they affect the intensity rather than the breadth of the reflection rings. This view is supported by the observation that the diffuse Preston-Guinier X-ray reflection spots due to heat vibrations in crystals are not affected by plastic deformation of the specimens; they should be quite sensitive to any extended irregular distortion of the lattice.⁹

If, in a particular case, both the above factors contribute simultaneously to the broadening, then the problem of isolating the contribution of each factor from the resultant is very involved. A special feature of the present work is that the contribution of variable internal strains has been minimized by utilizing the directional characteristics of the strains in suitably deformed specimens. This device was suggested by the results of Smith and Wood^{7,8} on residual lattice strains in metals, to the relevant features of which reference is made next. In this way it has been possible to determine the limiting crystallite size from the broadening then remaining.

2. Internal Strains.

It has been shown that after relatively homogeneous deformation, as in a tensile test prior to necking, the atomic lattice of a metal exhibits a system of residual strains which may be directional.⁸ The condition of the metal is described conveniently by reference to Fig. 1, which represents, say, the section of an iron tensile test-piece after plastic strain. The rectangles indicate grains of particular orientations;

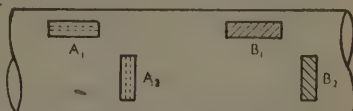


FIG. 1.—Residual Strain Exhibited by A Planes is the Same for all Grains A_1 , in which the A Planes are Parallel to the Surface; a Different Strain is Exhibited by Grains such as A_2 , when A Planes are Perpendicular to the Surface.

thus in A_1 a given set of atomic planes is parallel to the surface of a specimen, while in A_2 the same set is at right angles to the surface. The rectangles B_1 and B_2 are corresponding grains, but in these a different set of planes is respectively parallel and perpendicular to the surface.

It is then found that within limits of measurement, the residual strain in any given crystallographic direction is the same for grains of the same orientation. Thus the strain exhibited by the A planes, as measured by the percentage change in spacing from the initial unstressed value, is the same for all grains such as A_1 in which the A planes are parallel to the surface. We may refer to this group of grains as group A_1 . The value of the strain is different, however, from that shown by the A planes in another group, such as group A_2 in which the A planes are perpendicular to the surface.

The strain exhibited by the A planes in groups of orientation between the parallel and perpendicular positions varies in a regular manner between these two extremes. Corresponding variations in strain are exhibited by the B planes, but the magnitudes are different since a different direction in the unit cell is involved.

Each set of planes, such as the A planes or the B planes, produces a separate X-ray ring of which the diameter is fixed by the interplanar spacing. If experimental conditions are such that the A ring is formed by reflections from the A planes in differently oriented groups, then the reflection ring will be made up of a range of diameters, since the A planes in each group are in a different state of strain. The ring, therefore, will exhibit a broadening on that account. This is the broadening referred to in the previous Section as due to the factor of irregular lattice strains, and which must be allowed for before the contribution due to the factor of small crystallite size can be studied.

It is evident that the factor of irregular lattice strains can be minimized at once by choosing experimental conditions such that the A ring is formed by reflections from the A planes in one group only. The ring then may possess an expanded diameter or a contracted diameter, according to the sign and magnitude of the strain, but not a range of diameters. Therefore it would not exhibit a broadening due to the variation of internal strains in the specimen. Advantage was taken of this observation in the present work.

Fortunately the X-ray diffraction process lends itself to the required limitation. A reflection from a particular set of planes occurs only when the incident beam is inclined to the planes at a critical angle. Then if the beam is directed at a specific angle to the surface of the specimen it will automatically select for reflection a group of grains of the same orientation relative to the specimen and therefore in the same stage of

strain, which is the condition desired. In the present work, with the back-reflection technique, the group of grains utilized normally was that in which the set of planes under examination was virtually parallel to the surface. Other groups would give similar broadening of the reflection ring so far as the factor of small particle size is concerned.

Some scatter in the directionality of the internal strains is to be expected, since no deformation can be perfectly homogeneous. In practice, however, the scatter is not large in a tensile specimen prior to necking, or even in a cold-rolled specimen. The saving feature is that the diameter of the X-ray ring is not over-sensitive to elastic strains of the order met with in metals. The limit of sensitivity is the strain which would be produced by a stress of about 2 tons/in.² The degree of uniformity required in the deformation, therefore, is not critical, especially since the incident X-ray beam in practice covers only about 1 mm.² of surface at one time.

3. Test by X-Ray Rings from Cold-Worked Solid Metal and Filings.

It follows that a test of the above considerations can be made by comparing the breadth of the X-ray ring from cold-worked metal in the normal massive state with that from cold-worked metal which has been reduced to randomly oriented fragments, for instance by filing. For in the filings, grains originally of different orientation and therefore differently strained will be brought into a position to reflect simultaneously to the same reflection ring. The ring from the filings, therefore, should exhibit a greater diffusion than that from the solid metal, since the broadening due to the irregular lattice strains will be superposed on any broadening due to the factor of small crystallite size. Further, whereas the diameter of the ring from the solid metal may be expanded or contracted according to the group of grains reflecting, that of the ring from the filings should be the same as the diameter of the ring from the undeformed metal since, on the average, as many of the reflecting fragments will be in tension as in compression.

Such a comparison was carried out as part of the present work. It is of some importance also because, hitherto, various workers in studying the X-ray rings from cold-worked metals have confined their attention to filings, because of the convenience of X-ray technique, and then assumed that their observations equally described the cold-worked metal in the normal solid state.

The comparison was carried out on specimens of iron. The reflection rings from stretched tensile test-pieces were compared with those given under the same conditions of the X-ray test by filings from the same specimens. The action of filing might have imposed further cold

working, but the point is immaterial. The broadening of the rings reaches a limiting value with progressive cold work; this limit for heavily worked iron can be compared in the two conditions. Iron forms a suitable test material because after deformation the solid metal may exhibit large internal strains without showing excessive diffusion of the X-ray rings. Some materials, such as copper, exhibit relatively small residual strains but a marked diffusion of the X-ray lines; they would not provide so sensitive a test.

The iron was commercial 36-S.W.G. sheet with main impurities carbon 0.045, manganese 0.29, silicon <0.01, sulphur 0.012, and phosphorus 0.031%. Flat tensile specimens were stamped out with a parallel test-gauge $2\frac{1}{4} \times \frac{1}{2}$ in. They were first freed from internal strains by heating *in vacuo* at 950° C. for about 20 min. and cooling through the change point at a rate of 20° C./min. The specimens were then extended in a small straining machine until the X-ray photographs indicated that the maximum broadening of the rings had been attained. In general, this was after some 40% extension and just prior to necking. It was known from other work on similar iron deformed by cold rolling that the maximum broadening is reached after about 30% reduction, no appreciable change being produced by further reduction to 90% and more. This experience helped to indicate when the limiting line-breadth had been attained with the present specimens. It could be shown also by X-ray photographs taken after successive etches of the surface that the condition of the material at this stage was sensibly the same throughout the volume. For the comparison, the filings were formed into flat compacts so that they might be X-rayed under the same geometrical conditions as the flat solid specimens.

The X-ray photographs were obtained in a precision back-reflection camera from the (310) planes with $\text{CoK}\alpha$ radiation at a specimen-film distance of 10 cm. The incident beam was perpendicular to the surface of the test-specimen when this was stationary; in order to obtain continuous rings from the annealed material the specimens were oscillated in the usual way through a small angle about this position. For uniformity, the cold-worked specimens were oscillated similarly.

The breadth of the lines recorded on the film was measured by traversing with a Dobson microphotometer, and was expressed in the conventional way as the area under the density curve divided by the height of the curve at the peak. The correction of this breadth for the presence of the α_2 component of the $\text{K}\alpha$ radiation and for the finite width of the slit system are referred to later. For purposes of the present comparison it sufficed to take the breadth after correction for the α_2

component, and to take the difference between the breadth of the line from the cold-worked specimen and from the annealed specimen as a measure of the broadening due to the cold working.

This difference provides the required comparison between the solid metal and the filings for the condition of maximum broadening. The relevant measurements are set out in Table I. They show clearly that the broadening due to cold work when measured on the filings has practically double the value obtained from the solid metal. The

TABLE I.—*Comparison of Maximum Line-Broadening and Diameter of (310) Reflection Rings from Cold-Worked Iron in the Form of Solid Metal and of Filings.*

	Hardness, D.P.N.	Elongation, %.	Line-breadth, mm.	Ring dia., cm.
<i>Solid specimen :</i>				
Annealed	79	Nil	1.33	6.75
Cold worked	180	40	3.79	6.85
<i>Filings :</i>				
Annealed	1.33	6.75
Cold worked	6.71	6.75

difference is $6.71 - 1.33 = 5.38$ mm. for the filings as against $3.79 - 1.33 = 2.46$ mm. for the solid metal. The measurements show also, as predicted, that the over-all diameter of the diffraction ring from the filings is unchanged, whereas that for the solid metal is increased by as much as 1 mm. as a result of the cold working.

The experiments confirm the directional nature of the lattice strains in the uniformly deformed solid metal, and avoid the complication of introducing additional contributions to line-broadening by randomly oriented strains. Also they show that the common assumption that the line-broadening from filings is the same as from cold-worked solid metal is incorrect.

4. *Test of Possible Relation between Hardness and Internal Strains.*

It has been found that in general the hardness of a cold-worked metal is related to the broadening of the X-ray rings. As already indicated, unless special precautions are taken, the broadening may be due to a combination of the two factors of internal strains and small crystallite size. It will be shown in this Section that the hardness is not related to the internal strains.

The possibility of an unambiguous proof was again suggested by the directional nature of the internal strains in the solid cold-worked metal. Previously, the presence of such strains has been surmised from the broadening of the X-ray rings. But from the above-mentioned

considerations it is evident that the state of internal strain in the solid metal can be judged without reference to the broadening. It is necessary only to observe the diameter of the reflection rings.

For these tests the diameter of the X-ray rings from strain-hardened specimens was measured as the hardness was removed by heat-treatment. Measurements were made also of the line-broadening. The specimens employed were a further series of iron tensile test-pieces

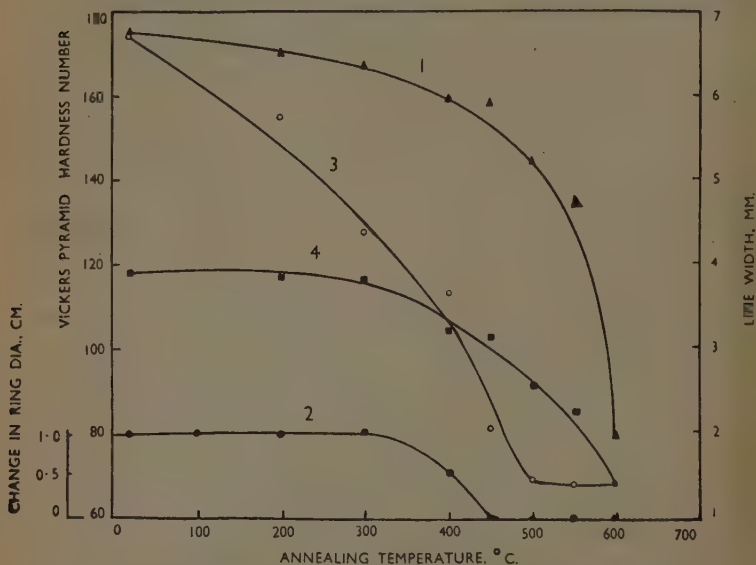


FIG. 2.—Variation with Annealing Temperature of (1) Hardness, (2) Internal Strain (Ring Diameter), and (4) Line-Broadening of Plastically Deformed Iron Specimens. Curve (3) shows the change in line width of specimen prepared by filing.

similar to those already described. After annealing they were extended by 30% to produce the same strain-hardened condition. Individual specimens were then heated *in vacuo* for 1 hr. respectively at 300°, 400°, 450°, 500°, 550°, and 600° C., recrystallization occurring at the last temperature. The hardness, line-breadth, and ring diameter were determined before and after heating. For curiosity, filings from each specimen were similarly heat-treated. The experimental conditions for the X-ray measurements were as described in the preceding Section.

The results are shown in Fig. 2. The hardness, change in ring

diameter, and degree of broadening for the solid specimens are plotted against temperature. The breadth of the rings from the filings is included. These curves lead to the following conclusions.

(1) The hardness and the broadening of the reflection rings from the solid specimens change with temperature in a similar manner. Both remain much the same up to 300°C . and then begin to fall, at first slowly and then rapidly in the range 500° – 600°C ., recovery of both being completed at the latter temperature, which was the temperature producing recrystallization.

(2) There is no relation between the hardness and the internal strains. The diameter of the diffraction ring, which indicates the state of strain, falls from an initial expanded value corresponding to a marked internal strain of some 0.04% to the normal value between 300° and 450°C . Thus the normal diameter is recovered before the main changes in hardness have begun.

(3) The broadening of the rings from the filings behaves as if it were the resultant of the two factors of internal strain and small crystallite size. On heating the specimens, the broadening falls more quickly than the hardness and is for the greater part removed at the temperature which removes the internal strains. The broadening then remaining is of the same order as that exhibited by the solid specimens at the same temperature. No precise conclusions are drawn from this curve because the degree of cold work attained by filing cannot be estimated. However, it confirms that the broadening of the rings from the filings is not representative of solid metal, and shows how confusion can arise if such X-ray observations are applied, unmodified, to consideration of normal metal.

It follows indirectly from these results that if, as many observations prove, the hardness is related to the broadening of the X-ray rings and the hardness is independent of the internal strains, then the hardness is related to the alternative cause of broadening, the small crystallite size.

5. Formal Definition and Determination of Line-Broadening.

In the following Sections the measurement of line-broadening will be considered in more detail. In this Section for completeness there are interpolated the formal definition of the line-breadth and the problem involved in its measurement. This has been discussed fully by F. W. Jones.¹⁰ The present note is inserted, however, because the treatment here differs in certain essentials which, it is thought, lead to a simpler and more accurate procedure. The details are of mathematical interest only and will be published elsewhere.

The problem is to find the broadening due to the cold-worked state of the specimen when that broadening in practice includes the effect of the finite width of the slit system which collimates the incident X-rays.

The effect of the finite slit system alone is given by the microphotometer traverse of the X-ray ring from an annealed specimen, in which the structure is assumed perfect. The profile of this traverse is represented in Fig. 3 by the curve S , the equation to which may be written $I = I_0 S(x)$, where I_0 is the peak. The breadth is now defined

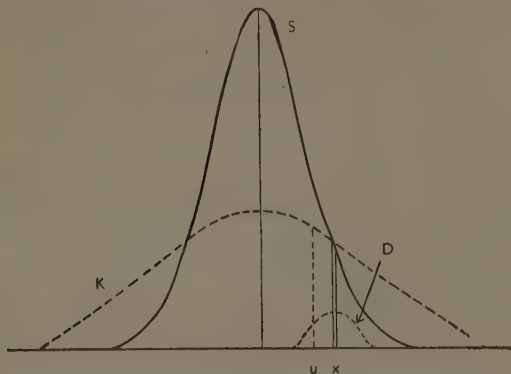


FIG. 3.—Diagrammatic Representation of Broadening of X-Ray Line. Shape of line from annealed specimen is S . The element at x broadens to shape D . Sum of those broadened elements gives final observed shape K . Problem is to find shape D from observed S and K .

as the area under the curve divided by the height at the peak and is therefore $b = \int S(x)dx$: the integral here, and throughout, represents a sum to infinity. Thus defined, the breadth depends on the shape and not the size of a curve.

The effect of broadening then is considered as follows. The required diffraction broadening is that given by a very thin slit. The finiteslit curve S is divided into thin rectangles, as drawn at x . Each will broaden to a similarly shaped curve $D(x)$ of intensity distribution $ID(x)$, where I is the peak of an elementary curve and is given at x in terms of $I_0 S(x)$ by equating the area under the curve, namely $\int ID(x)dx$, to the area of the rectangular element $I_0 S(x)dx$. The breadth of the elementary curve is then $\beta = \int D(x)dx$, the constant required.

The final observed curve K is the sum of the elementary curves. Thus the contribution of the elementary curve D to the ordinate of the final curve at $x = u$ is $ID(x - u)$. This leads readily to the resultant curve :

$$K(x) = I_0 \frac{\int S(x)D(x - u)du}{\int D(x)dx}$$

Its breadth is $B = \int K(x)dx$.

The problem then is to find $\beta = \int D(x)dx$ from the initial observed line-breadth b , the final observed breadth B , and from the shapes of the curves $S(x)$ and $K(x)$ given by the microphotometer traces.

Allowing for the constant terms we may write the relation above in the form :

$$K_1(x) = \int S(x)D(x - u)dx \quad . \quad . \quad . \quad (3)$$

In order to deal with this relation, Jones assumed particular functions for the unknown $D(x)$ and worked out a system of corrections which gave the required breadth in terms of the measured B and b . This corrected breadth, however, depends partly on the choice of function, which cannot be guessed with any certainty.

The procedure adopted in the present work is based on the observation that the relation (3) is essentially the Faltung integral of operational calculus, and if two of the functions K_1 , S and D are known, the third can be found simply from knowledge of their transforms.¹¹

In the present instance, the curves S and K were known from the microphotometer traces. The curve S was fitted perfectly by an

equation of the form $\frac{1}{1 + a^2x^2}$ and the curve K by a similar equation

$\frac{1}{1 + c^2x^2}$. By use of the Fourier transforms of these functions it can

be shown that the required $D(x)$ has a similar form $\frac{1}{1 + m^2x^2}$, and that :

$$B = \frac{\pi}{c}, \quad b = \frac{\pi}{a}, \quad \text{and} \quad \beta = \pi \left(\frac{1}{c} - \frac{1}{a} \right)$$

Thus the required breadth β was given by the simple relation $\beta = B - b$, when B and b could be obtained directly from measurement of the areas and peaks of the curves K and S given by the cold-worked and annealed specimens respectively.

This result is rather interesting because it was the correction first

suggested on empirical grounds by Scherrer in connection with his formula, and subsequently dismissed by most authors at sight because as a solution of the problem it appeared too simple.¹² It depends, of course, on the above forms for the known curves S and K , but these forms in the experience of the present authors are the ones most frequently encountered. This is confirmed also by other workers.¹³

It follows that for the most accurate measurements the experimental conditions should be such that in the X-ray photographs the breadth B from the cold-worked metal should be as large as possible and the value of b from the annealed metal as small as possible. This was obtained in the back-reflection technique by making the observations on rings for which the reflection angle θ was large, as required by relation (1) or (2) in Section III. 1. At the same time b was kept small by using a narrow slit of approximately 0.25 mm. width to define the X-ray beam and by use of carefully adjusted focusing conditions.

Finally, the usual correction was made for the fact that the X-ray rings are doublets which tend to overlap in the spectra from the cold-worked specimens. Particulars of the method actually followed have been published separately.¹⁴ It is not described here since various effective methods are well known.

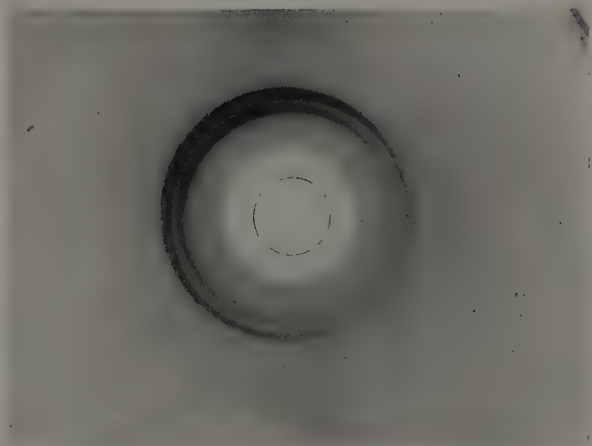
6. Short-Wave-Length Test for Small Crystallite Size.

The broadening due to small particle size is proportional to $\sec \theta$ and to the wave-length λ of the X-rays employed. That due to internal strains is proportional to $\tan \theta$ but independent of the wave-length. These observations follow from relations (1) and (2) in Section III. 1. It has been suggested by several authors that the cause of broadening in a particular instance might be distinguished by studying the variation with reflection angle or wave-length.

In practice it is doubtful whether the experimental arrangements normally employed have the necessary precision. In considering the variation with angle it is noted that $\sec \theta$ and $\tan \theta$ differ most when θ is small. But when θ is small the absolute value of the broadening itself becomes small; the quantity to be measured is then small compared with the geometrical correction due to the finite slit system, and is most subject to error. If both causes of broadening are present the criterion becomes of still less use. Attempts to utilize the different variations with λ have been made in experiments on cold-worked copper by Stokes, Pascoe, and Lipson,¹⁵ and independently by Dehlinger and Kochendörfer,¹⁶ with results which are contradictory.



4

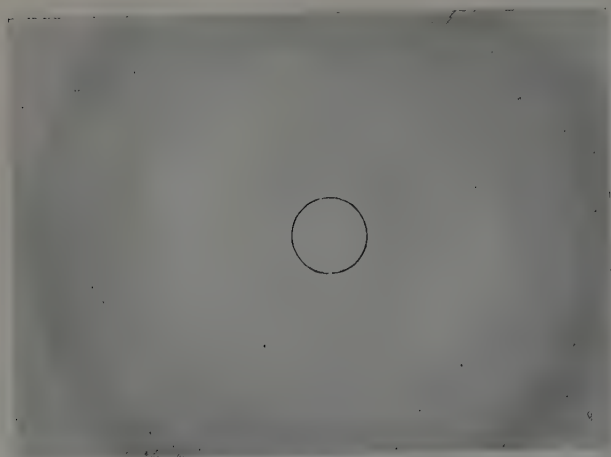


5

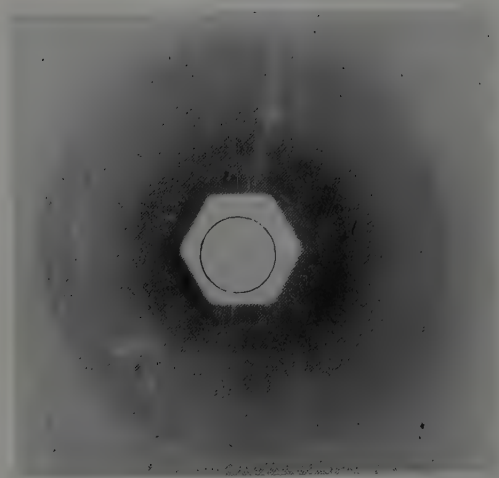
FIGS. 4-5.—X-Ray Reflections from Aluminium Single Crystal Before (Fig. 4) and After (Fig. 5) Heavy Deformation, Showing Spread of Reflections which may Result.

[To face p. 584.

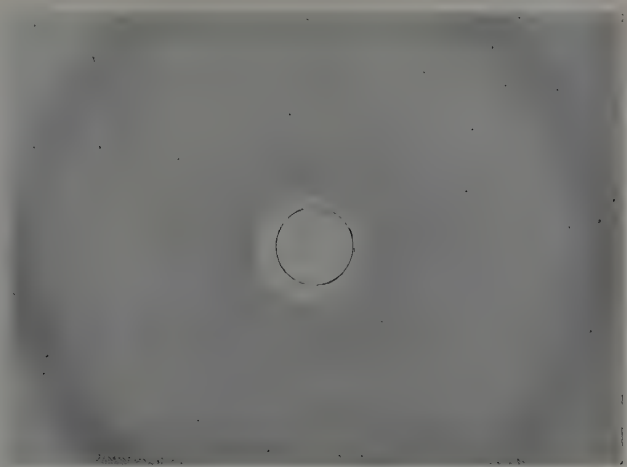
6



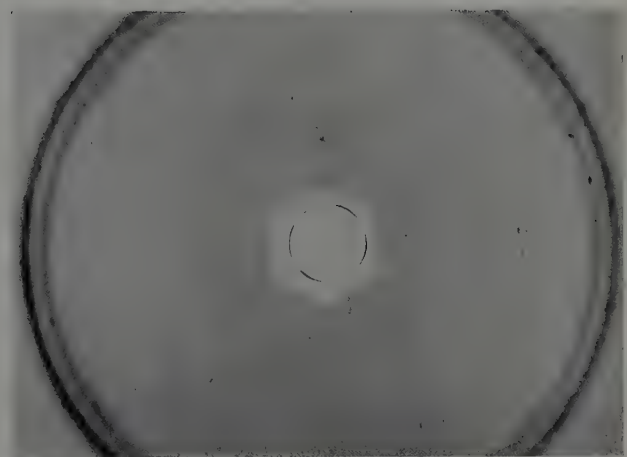
7



FIGS. 6-7.—X-Ray Back-Reflection Rings from Heavily Worked Tungsten Photographed with Long (Fig. 6) and Short (Fig. 7) Wave-Lengths, Showing that Line-Broadening Depends on Wave-Length.



8



9

FIGS. 8-9.—X-Ray Back-Reflection Rings from Heavily Ground Surface of Tungsten Before (Fig. 8) and After (Fig. 9) Slight Etch, Showing Shallowness of Cold-Worked Surface Layer.

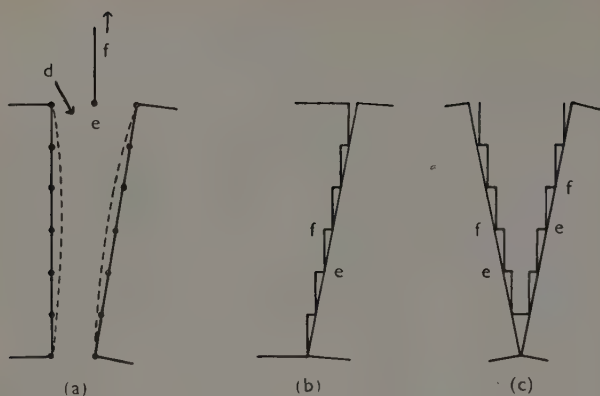


FIG. 10.—Diagrammatic Representation of Boundaries Between Crystallites of Different Angular Tilts. Length of crystallite is $L = ef$, and d is an interatomic distance.

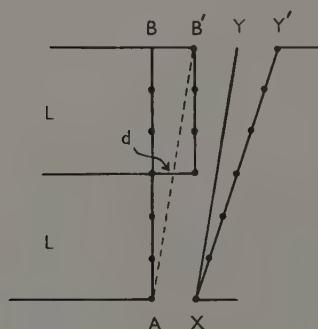


FIG. 11.—Diagrammatic Representation of Slip Made Possible by Accommodation at Boundaries of Crystallites After Shear d/L . Initial boundaries are AB and XY . After shear, boundaries are AB' and XY' . Crystallite on left then has alternative of deforming by a slip movement.

Similarly, it is difficult to obtain conclusive results by the wave-length criterion with the wave-lengths normally used for X-ray diffraction, which lie between approximately 2 and 1.5 kX. Longer wave-lengths are too quickly absorbed. Much shorter wave-lengths are avoided because the efficiency of reflection is reduced at large reflection angles, especially at the very large angles essential for accurate measurements of the broadening. In fact, back-reflection photographs with very short wave-lengths of the order of 0.5 kX. have been regarded as impracticable.

It is evident, however, that the use of such short wave-lengths for back-reflection photographs, if successful, would provide a clear-cut criterion. The same cold-worked specimen could be photographed at a sensitive high-reflection angle first with a normal wave-length of the 2-1.5 kX. range, and then with a short wave-length of, say, 0.7 kX. If the broadening were due predominantly to small particle size, it would decrease by a factor of two to three times. If due to internal strains, it would be unchanged. The difference would be unmistakable. In view of this application the practicability of X-ray back-reflection photographs from heavily cold-worked metals has been studied by one of the present authors (W. A. Wood) and found to be quite feasible.² He was able to show a marked change in the line-breadth exhibited by a cold-worked steel when photographed by $\text{CoK}\alpha$ and $\text{MoK}\alpha$ radiations, wave-lengths 1.8 and 0.7 kX., respectively. (An attempt to repeat this experiment by Lipson and Stokes failed¹⁷; their negative result might have been anticipated, however, because they used iron in the form of filings which, as shown in Section III. 3., introduces unnecessary complications due to random internal strains.)

The test has been developed further and applied to the metals iron, molybdenum, tantalum, and tungsten, used in the present investigation. Quantitative measurements were made of the line-broadening exhibited by these metals before and after cold working, first with the appropriate long wave-length and then with the short $\text{MoK}\alpha$ radiation wave-length. The line-broadening due to the cold working as shown by the two wave-lengths is given in Table II. The X-ray measurements refer to the maximum broadening obtainable by progressive cold working, and for each metal were made on the same specimen under the experimental conditions already indicated. The broadening given is the true broadening β discussed in the preceding Section, and is expressed in the accepted way in terms of the angle subtended at the specimen by the broadening on the film.

It is evident from Table II that the measured line-broadening is reduced to a striking degree on going from the long to the short wave-

TABLE II.—*Line-Broadening Due to Cold Work, Measured on Same Specimens with Long and Short Wave-Length Radiations.*

	Wave-length, kX.	Plane.	θ	Line-broadening, radians.
<i>Iron :</i>				
Long	1.785	310	80.5°	0.036
Short	0.708	732	76.9°	0.010
<i>Molybdenum :</i>				
Long	1.658	321	80.3°	0.023
Short	0.708	743	75.9°	0.006
<i>Tantalum :</i>				
Long	1.541	411	81.7°	0.045
Short	0.708	910	76.7°	0.010
<i>Tungsten :</i>				
Long	1.658	321	78.5°	0.028
Short	0.708	752	81.5°	0.014

length. The predominant cause of the line-broadening is therefore the factor of small crystallite size. Any effect of random lattice strains has been rendered inappreciable.

It can be shown further that the line-broadening is in fact proportional to the wave-lengths, as would be required by the Scherrer relation (1) in Section III. 1. For exact comparison the broadening should be measured by each wave-length at identical values of the reflection angle θ , when the broadening should be exactly proportional to the wave-lengths. In practice, the angles differ by a few degrees. The difference is too small to affect the issue, but the effect can be allowed for if necessary. The broadening due to small particle size is proportional to $\sec \theta$ as already noted, and the appropriate correction can be made by multiplying by the ratio of the secants. In Table III the broadening measured by the short wave-length has been corrected in this way to bring it to the value it would have at the same reflection angle as that characterizing the long wave-length. In the same Table the ratio of the wave-lengths used for each metal is given. It is evident that the broadening measured by the two wave-lengths is in the same ratio as the wave-lengths, to a near approximation. In passing, it may be noted that the secants and tangents differ so little at the large reflection angles that the ratio of the tangents could have been taken without affecting the results; the tangent would have been appropriate for broadening due to internal strains.

The short-wave-length test may be applied rapidly by noting the resolution of the α_1 and α_2 components of the reflection rings. If the operative cause of the broadening is predominantly that of small

TABLE III.—*Line-Broadening Observations in Table II Corrected for Differences in θ .*

	Line-broadening, radians,	Ratio.	Wave-length ratio.
<i>Iron :</i>			
Long wave-length . . .	0.036	2.6	2.5
Short " . . .	0.014		
<i>Molybdenum :</i>			
Long " . . .	0.023	2.6	2.3
Short " . . .	0.009		
<i>Tantalum :</i>			
Long " . . .	0.045	2.8	2.2
Short " . . .	0.016		
<i>Tungsten :</i>			
Long " . . .	0.028	2.5	2.3
Short " . . .	0.011		

particle size the difference is so marked with the large change in wave-length employed that the degree of resolution of the doublet may be used to indicate the apparent broadening at once by inspection. Allowance has to be made for the fact that the angular separation of the components is somewhat greater for the short wave-length. This is easily done by reducing the specimen-film distance for the photograph with the short wave-length by an appropriate amount. The linear separation on the film can thus be brought to the same order. This has been done in Figs. 6-7 (Plate LXVII), which are photographs of the same cold-worked specimen of tungsten by $\text{NiK}\alpha$ and $\text{MoK}\alpha$ radiations, wave-lengths 1.658 and 0.708 kX., respectively. It is seen at once that the α_1 and α_2 components, which with the long wave-length have diffused almost into a single halo, are still sharply resolved with the short wave-length. Tungsten provides a critical test because reflection of the short wave-length occurs at the larger reflection angle, at which any tendency to diffusion would be enhanced.

Application of the short-wave test to the metals used in the present work was essential. As already explained, the effects of internal strains on the broadening have been minimized by taking advantage of their directional character. Of the metals under examination only iron was available in a form from which tensile test-pieces could be obtained and extended in a reasonably uniform manner. The molybdenum and tantalum were in small sheet form which, after the preliminary anneal, had to be deformed by cold rolling. The tungsten was worked by swaging and drawing at temperatures as low as possible, but it was not easy in this way to get deep penetration of the cold-work effects, and the most

satisfactory results in this respect were obtained finally by compression of small specimens in an Amsler machine. The specimens showed fine cracks but not enough to affect the surface for the X-ray measurements. The above-mentioned experiments on these metals with the long and short wave-lengths were essential, therefore, in indicating that even with these modes of deformation the internal strains, if present, were sufficiently directional not to contribute measurably to the broadening of the X-ray rings.

The observed tendency of tungsten to resist the penetration of cold-work effects may throw light on the X-ray results of Smith and Stickley on this metal.¹⁸ They claimed that the broadening due to cold work in their specimens was due to internal strains. Their tests were made by measuring the broadening at different reflection angles with the conventional long wave-lengths. As already remarked, these tests produce relatively small changes compared with possible experimental error. In their experiments the cold working was produced by surface grinding of the specimens. The present authors repeated this procedure with various modes of grinding and polishing, and found that the depth of layer affected was exceedingly thin. The layer was thin enough to be penetrated even by the long wave-lengths, and therefore as an example of cold-worked metal could not be regarded as satisfactory for X-ray investigation. The effect is illustrated by Figs. 8-9 (Plate LXVIII), which are back-reflection photographs with $\text{NiK}\alpha$ radiation, first of a ground surface and then after not more than 0.001 in. had been removed by etching. It is surprising to note how completely this slight etch removed the diffusion of the rings associated with the ground surface.

In concluding this Section it should be noted, perhaps, that in future tests on some metals the internal strains may be found insufficiently directional even after homogeneous deformation. In such cases it will be very difficult to separate with any accuracy the contributions to the broadening of the individual factors of internal strain and small crystallite size. However, so far as the metals under investigation are concerned, the measurements given above show that the broadening obtained with the device employed is primarily due to the small crystallite size produced by the cold working. The measurements of this broadening can be used directly for computation of the crystallite size of these metals.

7. Numerical Values of the Crystallite Size.

The values for the maximum broadening produced by cold working were given in Table II. From these values the numerical values of

the corresponding crystallite size were obtained by direct substitution in the Scherrer formula. The results are given in Table IV, results obtained by use of the long and the short wave-lengths being recorded separately.

TABLE IV.—*Limiting Crystallite Sizes Derived from the Values of Line-Broadening Recorded in Table II.*

	Long Wave-Length.	Short Wave-Length.
Iron	3.0×10^{-6} cm.	3.1×10^{-6} cm.
Molybdenum	4.2 "	4.8 "
Tantalum	2.4 "	3.1 "
Tungsten	3.0 "	3.3 "

The crystallite sizes obtained with the different wave-lengths for the same metal are in good agreement. The figures given by the long wave-length will, however, be taken, as nearer to the probable values rather than the mean, because they are obtained from the broader and therefore more easily measured X-ray rings.

These sizes may usefully be compared with some recent important measurements on the fine structure of cold-worked metals made by C. S. Barrett²⁵ with the aid of the electron microscope. Although this technique involves uncertainties, owing to the necessity for using replicas of the surface, it leads to interesting observations. Barrett confirms the existence of a sub-structure in the metallic grain as foreshadowed by the X-ray work. Also he finds that the size of the elements is of the same order as that already deduced by the latter method. Thus the value for fine pearlite is given as 5×10^{-6} cm.

Other exploratory X-ray measurements were made some years ago by Wood⁴ on various metals including iron and molybdenum. The results were of the same order as the values for these metals in Table IV but rather larger. The reason is that in order to reduce uncertainties due to possible internal strains, the nature of which became clear only after the subsequent work on lattice stress-strain curves mentioned in Section III. 2., the early measurements were purposely confined to cold-worked metals in a partially recovered condition and therefore not at their hardest. The figures in Table IV refer to the limiting size after severe cold working and represent the values required for correlation with the ultimate strength.

IV.—DISCUSSION : CRYSTALLITE SIZE AND STRENGTH.

1. *Limiting Elastic Strain.*

Theories of deformation have concentrated on the mechanism of slip. This process is intriguing because of its apparent simplicity and because in a perfect lattice it should not occur under stresses which are effective in practice. In explanation, the main line of attack has been to postulate particular kinds of flaws and some interaction leading to a tractable mathematical model, and then to estimate the stress required to start a disturbance. In this way it has been possible to explain the weakness of a metal. However, so far, it has not been possible to discover, firstly, why plastic flow should strengthen the metal again; and, secondly, why on any picture of flaws the strength of a metal should be at all reproducible. It is possible that the slip process of itself never will account for these phenomena.

There is evidence that the mechanism of deformation is more complicated than the slip process would suggest. It was pointed out, for instance, in the early papers by Wood,⁴ Gough and Wood,¹⁹ and Smith and Wood⁵ that the slip was accompanied by a fragmentation of the grains which began at the yield stress and reached a limiting size at the ultimate stress. The slip and fragmentation appeared to be related. In view of the limit to fragmentation it was suggested that there might well be a limit also to the capacity of a metal to accommodate itself to change in shape simply by slip, when the strength would be set by the limiting elastic strain which the crystallite would exhibit when incapable of further breakdown.

Thus, the dispersion to crystallites would appear to supplement the classic observations on deformation by slip, with the addition of the quantitative aspect provided by the measurements on crystallite size.

As measurements of the limiting size were made, it became evident that the size was such that at stresses corresponding to the ultimate strength of the various metals the crystallite would elongate by approximately one interatomic distance. This is a fundamental observation defining a critical elastic strain. An interpretation of this point is advanced later.

Suggestions as to why a structural element should *yield* at a strain of approximately one atomic distance have recently been put forward by Orowan,²⁰ Bragg,²¹ and Rohner²²; also by Duwez in an early paper on secondary structures.²³ The most direct treatment is by Bragg, whose criterion for slip is that the elastic strain energy in a block after slip must be less than before slip. This criterion leads to a limiting shear strain of $d/2L$, where L is the side of the block and d the atomic spacing

in the slip direction; and therefore to a yield stress of $Gd/2L$, where G is the rigidity modulus. In his earlier papers Bragg substitutes for L the early figures for crystallite size published by Wood and shows that the yield stresses thus estimated are of the orders observed. In a later paper he uses Wood's figures to calculate some other form of glide region,²⁴ an interpretation apparently based on X-ray work by Stokes, Pascoe, and Lipson on cold-worked filings.¹⁵ It is suggested, however, in a previous Section that observations on filings cannot be safely extended to solid metal. Therefore in this paper the idea is retained of the crystallite produced by fragmentation.

The criterion based on strain energy, as Bragg points out, cannot be applied without consideration of the energy involved in the formation and movement of the flaws which make slip possible. When this factor is considered the criterion loses its initial simplicity. Moreover, these criteria refer to the primitive yield; but in practice this yield may vary widely, as from a single metal crystal to a fine-grained aggregate. Nor do the criteria lead to any clear explanation of strain-hardening.

The common point, however, is the fundamental observation that a structural element may become unstable when it increases one dimension elastically by an atomic diameter. Then if, as suggested by the X-ray work, there is a limiting crystallite size for a metal, it follows that there is a limiting elastic strain.

2. Strain-Hardening : Estimate of Ultimate Strength.

It is considered that the limiting crystallite size and elastic strain are to be associated with the ultimate strength of a metal rather than the yield. This view, coupled with the concept of fragmentation, then leads to a natural interpretation of strain-hardening as follows.

Firstly, the implication of the crystallite sub-structure in a grain should be considered. The chief feature is that in order to maintain any difference of angular tilt between neighbouring crystallites, the boundary between them must be of the form suggested in Fig. 10 (a) (Plate LXIX), where a line of atoms such as ef is introduced when the separation between the boundary layers of atoms becomes equal to an atomic distance. In three dimensions the line would be a plane of which ef is the trace. The boundary atoms themselves will, of course, take up intermediate positions as indicated by the dotted lines. This local distortion, however, will not affect the relative tilt of the body of the crystallites. A more extended picture of this type of boundary is given by Figs. 10 (b) and 10 (c) (Plate LXIX). If we consider the limiting

crystallite as the smallest stable unit and the side L of the unit therefore as the nearest distance of approach of centres of disturbance such as e , then the relative tilt of the crystallites will tend to the angle d/L radians. If d is taken as 3×10^{-8} cm. and L from Table IV as 3×10^{-6} cm., the tilt becomes about $\frac{1}{2}^\circ$, which is of the order suggested by various observers for the mosaic structure of crystals. It will be noted that a difference of many degrees will soon be built up across a grain, if the crystallites change in orientation progressively in steps of $\frac{1}{2}^\circ$. This is the condition noted by X-rays in the cold-worked metal.

Next, it may be seen that a critical elastic strain might be anticipated without reference to energy changes. It is known that in an isolated grain slip may take place at very low stresses. Other things being equal, it should take place under equally low stresses when the grain is part of an aggregate. The fact that it does not, means that the constraints imposed on an element of structure by its neighbours constitute an over-riding factor; the condition for slip in that element becomes determined by whether the surrounding matrix can accommodate the accompanying change in shape. Thus, under stress, the space occupied by the element must be such that it may be filled either by the element undergoing elastic strain in the same manner as the surroundings, or alternatively, by undergoing a slip jump. Now the elastic strain may change continuously with stress, but slip must occur in discontinuous jumps of one atomic distance. It follows, therefore, that there will be no room for the slip jump until the matrix has changed the shape of the element by the nearest equivalent elastic strain. For an element of side L in a crystallite formation deformed elastically by shear it is evident from Fig. 11 (Plate LXIX) that the strain required by this criterion of accommodation is also $d/2L$, where d is the atomic distance.

It will be noted that the above-mentioned view assumes that deformation of a metal is intrinsically non-homogeneous; that one element of a grain may deform elastically while a neighbouring part deforms plastically. This condition is required by a number of other considerations.

The process of strain-hardening then follows from the decrease in size of the elements, observed in the X-ray work as fragmentation. The smaller the element the greater the strain $d/2L$ required for slip.

Thus in the early stages of deformation, while the structure is reasonably uniform, a slip movement may traverse a whole grain, since accommodation can be found in general at the gross misfitting boundaries of differently oriented grains, or, in single metal crystals, on the free surface. In effect the quantity L then is large. The initial breakdown observed is to elements of the order of 10^{-4} cm. in size, which would lead to a critical stress of a few tons/in.² only. This initial yield

will depend, however, in an unpredictable way, on grain-size, orientation, and perfection.

In the later stages of deformation, when the grains themselves become dispersed into elements of varying orientation, the effective value of L will decrease. The critical elastic strain in shear will tend to a limiting value of $d/2L$ when L is now the lower limiting size. The corresponding shear stress will be $Gd/2L$. The ultimate tensile stress will tend therefore to the value Gd/L .

The values thus estimated for the metals under examination are given in Table V. The value taken for d is the atomic spacing in the slip direction [111]. The figure for G is the shear modulus in the slip direction. This is available from measurements on large single crystals for iron, molybdenum, and tungsten, but not for tantalum. In this metal, it has been necessary to take the modulus as measured on the bulk metal; this value is likely to be higher than in the slip direction, so that the calculated strength for tantalum is probably somewhat on the high side.

Values for observed tensile strengths are included in Table V for comparison, but it is not easy to find true measured stresses. The figures given in the literature refer mostly to nominal stresses calculated on the original cross-section. There is no universally accepted definition of tensile strength. For the present purpose it would be defined as the

TABLE V.—*Comparison of Observed Ultimate Tensile Strengths with Those Calculated from the Relation $S = Gd/L$, where L is the Limiting Crystallite Size, d the Atomic Spacing in Slip Direction, and G the Shear Modulus.*

	L , cm.	d , cm.	G , tons/in. ²	S (calculated).	S (observed).
Iron . . .	3.0×10^{-8}	2.48×10^{-8}	3.9×10^3	32 tons/in. ²	30 tons/in. ²
Molybdenum	4.2 "	2.72 "	8.6 "	56 "	75 "
Tantalum .	2.4 "	2.85 "	4 "	47 "	58 "
Tungsten .	2.9 "	2.74 "	10 "	95 "	110 "

stress which produces the largest observable elastic strain, but in mechanical tests there is no zero from which to measure the strain. Thus an elastic strain may be produced which is high under tension because the material is one which initially is in partial compression; hard-drawn wires, the surface layers of which often exhibit quite high compressive strains, would come into this class. The values in the Table, except for the iron which was tested directly, have been obtained from published tensile tests on annealed material where elongations also have been recorded, and therefore refer within the information

available to actual tensile strengths. These figures serve to indicate, however, that the calculated stresses definitely are of the right order.

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PURE PLATINUM, OF HIGH RECRYSTAL-1170 LIZATION TEMPERATURE, PRODUCED BY POWDER METALLURGY.*

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SYNOPSIS.

Previous work on the powder metallurgy of platinum is briefly reviewed. Hitherto no essential difference has been noted between the physical properties of sintered pure platinum and of melted and cast pure platinum. It is now shown that by the sintering and hot working of a fine powder compact of pure platinum, at a temperature considerably below its melting point, followed by severe cold drawing to wire, the fibrous structure of the resulting wire is made to persist when heated at temperatures well above the recrystallization temperature of wire produced from melted, cast, and similarly worked pure platinum. The increased stability of the fibrous structure of the sintered platinum wire is attributed to a small amount of suitably dispersed porosity, which has the effect of hindering recrystallization. The sintered platinum wire is, moreover, shown to possess greater resistance to elongation under tensile stress at high temperature, and greater resistance to intergranular corrosion, than wire from melted and cast platinum which has recrystallized at the temperature of testing. At relatively high temperatures the fibrous structure of sintered platinum wire is found to change to columnar.

I.—INTRODUCTION.

PLATINUM, in the refined state, is usually produced as a grey powder or sponge by the ignition of the salt, ammonium chloroplatinate. The high melting point (1774° C.) of platinum was a disadvantage in the early fabrication of platinum vessels, but powder metallurgy enabled sound metal to be produced in the form of ductile sheet and wire. Details of powder procedure were published in 1800 by R. Knight,¹ in 1805 by A. Tilloch,² and in 1829 by W. H. Wollaston.³ In 1931, D. McDonald⁴ stated that the sponge ingots, provided that they were made from pure platinum, handled in a proper manner, and sufficiently annealed, were physically and metallurgically superior to the usual unalloyed melted and cast metal, and could be drawn or rolled perfectly satisfactorily. Atkinson and Raper⁵ noted that the powder method obviated gas contamination and the picking up of impurities from refractories such as occur during melting, and was, therefore, an important process where it was necessary to maintain the metal in the

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highest state of purity. C. S. Sivil⁶ stated that a very thorough forging of sponge ingots above a temperature of 1000° C. was necessary in order to get rid of porosity, otherwise the resultant sheet showed blisters. Apparently the ultimate aim of the powder methods in all the cases cited was the production of metal with the minimum of porosity and maximum ductility. No essential distinction was envisaged between the physical properties of sintered and of melted and cast platinum of equal purity.

For certain purposes, porosity in a metal may be very useful, as for example in bearings,⁷ filters,⁸ and aircraft liquid de-icing equipment,⁹ and powder metallurgy provides a convenient means of ensuring the right amount of porosity and its correct dispersion. Such porosity is visible under the microscope and has the result of lowering the strength of the metal. However, for the stated applications strength is not a main factor. In general, the smaller the porosity of a sintered metal powder compact, the greater the tensile strength and ductility. Hence, if the sintered metal is required to have mechanical properties comparable with the cast metal, there will be a limit to the amount of porosity permissible in the sintered metal. It will be shown how a relatively small amount of porosity may be so highly dispersed as not to affect adversely the mechanical properties of cold-worked platinum, yet be capable of influencing the structural changes on heating.

II.—EXPERIMENTAL PROCEDURE.

1. *Production of Severely Cold-Drawn Wires from Platinum Powder.*

In order to compare the properties of sintered platinum with melted and cast platinum, both were produced from the same batch of platinum powder in the final form of cold-drawn wires, with a fibrous structure resulting from a cold reduction of 92% in cross-sectional area without intermediate annealing. In this paper the term "sintered platinum" is applied to such wires produced from platinum by a powder procedure. The powder metallurgy of platinum followed the procedure of (a) cold pressing, (b) sintering at a definite temperature, and (c) hot working at a definite temperature, with the object of producing metal which could be severely cold worked. In order to obtain a material suitable for pressing to a uniform compact, the platinum powder was sifted through a 90-mesh screen and any coarse particles were discarded, before loading into a rectangular steel mould. Compacting pressures of from 5 to 20 tons/in.² were used and compacts produced to the dimensions $2 \times 0.50 \times 0.50$ in., or $3 \times 0.75 \times 0.75$ in.

Sintering was conducted in an electrically heated alundum tube furnace, the compacts being heated from room temperature, maintained for 1 hr. at the selected sintering temperature, and finally allowed to

cool in the furnace. Each compact was measured before and after sintering in order to ascertain the volume contraction. Sintering temperatures ranged from 900° to 1500° C. and sintering was conducted either in air, dry nitrogen, dry hydrogen, or *in vacuo*.

Hot working of each sintered compact was carried out at approximately the same temperature as for sintering. The first operation was swaging to 0.25-in.-dia. rod, followed by hot rolling to 0.16 in. square rod. Pickling in hydrochloric acid was used to remove surface contamination from the platinum, which was then cold rolled and drawn to 0.047-in.-dia. wire without intermediate annealing. The melted platinum for comparison tests was produced from the same batch of platinum powder, which was melted in air in an alumina crucible in a high-frequency furnace. The 0.75-in.-dia. ingot was hot worked at 900° C. down to 0.16 in. square rod which was finally cold rolled and drawn to 0.047-in.-dia. wire. The term "regular" is used for this platinum in the paper.

2. Comparison of the Properties of Sintered and Regular Platinum.

For the purpose of comparison the following investigations were carried out on cold-drawn wires of each kind of platinum: (a) annealing tests at temperatures from 500° to 1700° C.; (b) microscopic and X-ray diffraction examinations; (c) hardness determinations; (d) tensile tests; (e) density determinations; (f) electrical-resistance measurements; (g) time-to-rupture tests at 700° C.; and (h) tests on high-temperature corrosion by lead.

III.—EXPERIMENTAL RESULTS.

1. Spectrographic Analyses of Platinum Powders.

The analyses of the various batches of platinum powders used in the investigations are given in Table I and relate only to the impurities present, the actual platinum contents not being determined. The major impurities are metals of the platinum group, namely rhodium, ruthenium, iridium, and palladium which are capable of forming solid solutions with platinum. The base metals are present in extremely small amounts. Most of the investigations were made on the purest batches and the results confirmed by occasional tests on the remaining batches. It was found that platinum of high recrystallization temperature could be produced by powder metallurgy from each batch of platinum, hence it may be assumed that the analytical differences had no effect on the behaviour of the batches.

2. The Porosity of Sintered Platinum Powder Compacts.

The porosity of the compacts depended principally on the compacting pressure and the temperature of sintering. Compacts which were

TABLE I.—*Spectrographic Analyses of Platinum Powders.*

Batch No.	Percentage of Element.					
	Rh	Ru	Ir	Pd	Au	Ag
1	0.001	<0.01	<0.01	0.001	Sl. Tr.	0.0001
2	0.001	<0.01	<0.01	<0.001	<0.001	0.0001
3	0.010	<0.01	<0.01	0.001	<0.001	0.0003
4	0.002	<0.01	<0.01	0.030	0.002	0.0001
5	0.013	<0.01	0.030	0.020	0.001	0.0001
6	0.013	0.020	0.030	0.024	0.002	0.0001
	Bi	Pb	Fe	Ni	Zn	Cu
1	<0.0001	0.0001	0.001	0.0001	Sl. Tr.	0.0003
2	<0.0001	0.0001	0.001	0.0002	<0.001	0.0003
3	0.0001	0.001	0.001	0.0003	0.001	0.0001
4	0.0001	0.0001	0.005	0.0001	<0.001	0.001
5	<0.0001	0.0029	0.002	0.0003	<0.001	0.0003
6	<0.0001	<0.0001	0.001	0.0003	0.0003	0.001
	Ca	Mg	Si	Sn	Sb	
1	Sl. Tr.	Sl. Tr.	Sl. Tr.	<0.0002	<0.003	
2	Tr.	Tr.	Tr.	<0.0002	<0.003	
3	Sl. Tr.	Sl. Tr.	Sl. Tr.	<0.0002	<0.003	
4	Tr.	Tr.	Tr.	<0.0002	<0.003	
5	Tr.	Tr.	Tr.	0.002	<0.003	
6	Tr.	Tr.	Tr.	<0.0002	<0.003	

Tr. = Trace.

Sl. Tr. = Slight Trace.

pressed at 15 tons/in.² had a density of approximately 14 g./cm.³, corresponding to a volume porosity of about 35%. Sintering for 1 hr. resulted in volume contraction with diminution of porosity as indicated in Table II. For a short period of sintering, such as 1 hr., the type of sintering atmosphere had no significant effect on the amount of porosity.

TABLE II.—*The Porosity of Sintered Platinum Compacts.*

Temperature of Sintering for 1 hr., °C.	Volume Contraction, %.	Density, g./cm. ³	Volume Porosity, %.
900°	3.6	14.5	32
1100°	7.5	15.1	29
1400°	14.7	16.4	24
1500°	19.3	17.4	19

Fig. 1 (Plate LXX) shows the distribution of porosity in a compact sintered at 900° C. in an atmosphere of hydrogen. Electrolytic etching¹⁰ did not indicate the occurrence of recrystallization or grain growth.

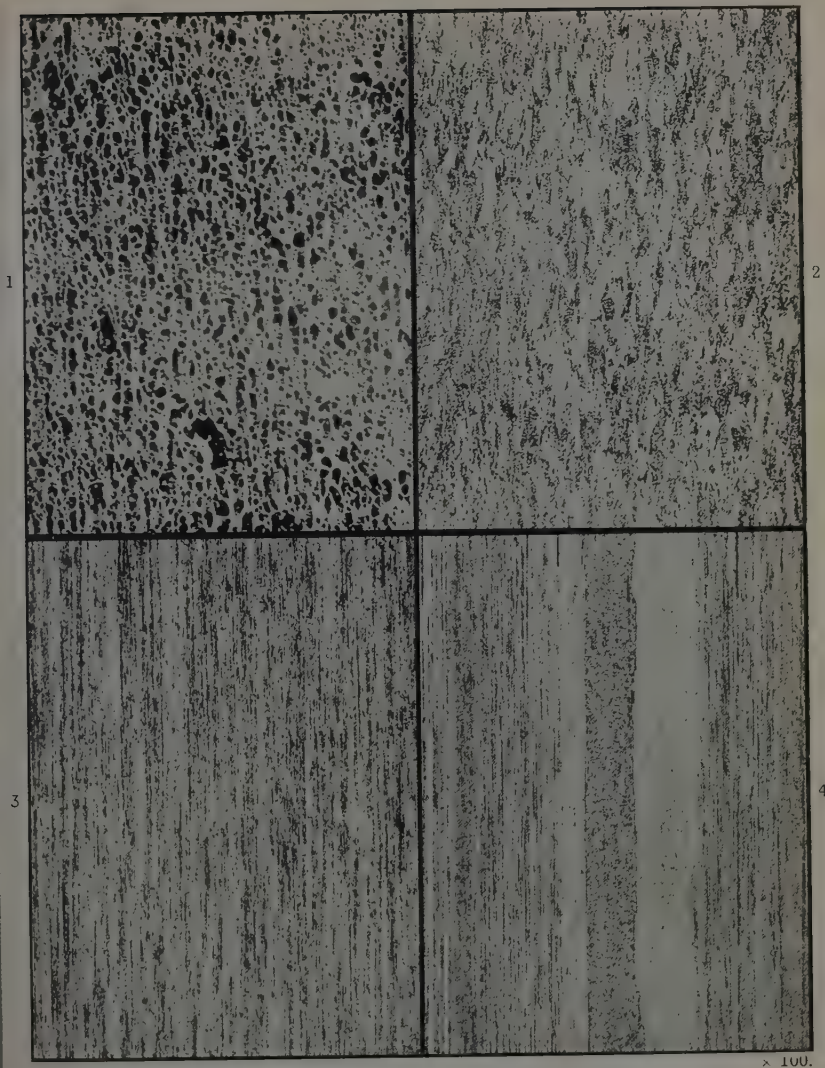


FIG. 1.—Structure of Platinum Compact After Sintering at 900° C.
 FIG. 2.—Structure of Compact After Swaging and Rolling at 900° C. Etched.
 FIG. 3.—Structure of 92% Cold-Drawn Wire. Etched.
 FIG. 4.—Structure of Wire After 15 min. at 1200° C. Etched.

[To face p. 598.]

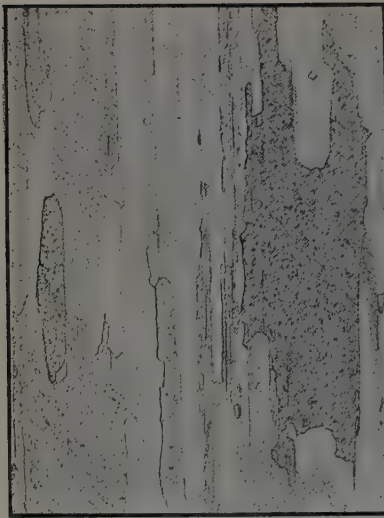


FIG. 5.—Structure of Wire from Compact Sintered at 1400°C ., After 15 min. at 1200°C . Etched. $\times 100$.



FIG. 6.—Structure of Wire from Regular Platinum, After 15 min. at 1200°C . Etched. $\times 100$.

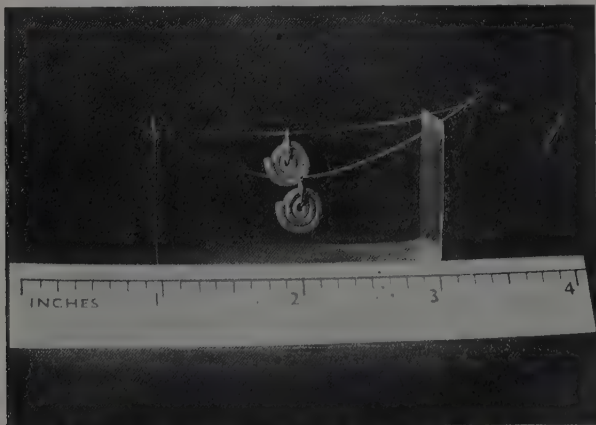


FIG. 7.—Sintered and Regular Platinum Alloy Wires After Lead Corrosion Test under Load at 800°C .



FIG. 8.—Fracture of Sintered Platinum Wire After Time-to-Rupture Test at 700° C.
Etched. $\times 100$.

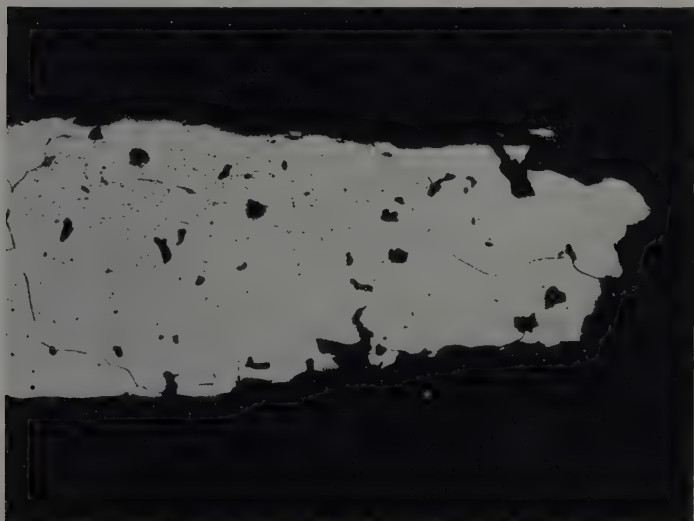


FIG. 9.—Fracture of Regular Platinum Wire After Time-to-Rupture Test at 700° C.
Etched. $\times 100$.

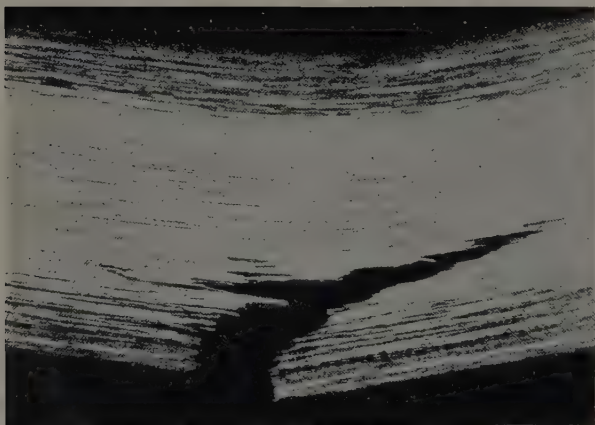


FIG. 10.—Longitudinal Section of Sintered Platinum Alloy Wire After Lead Corrosion Test and Bend Test. Etched. $\times 100$.

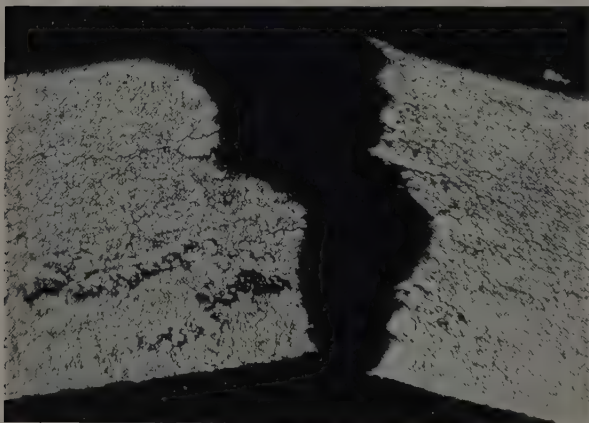


FIG. 11.—Longitudinal Section of Regular Platinum Alloy Wire After Lead Corrosion Test and Bend Test. Etched. $\times 100$.

3. The Structures of the Hot-Worked Compacts.

After hot swaging and rolling, the sections of the hot-worked compacts showed small amounts of microscopically visible porosity and on etching gave evidence of directional deformation. Fig. 2 (Plate LXX) shows the structure of a compact sintered at 900° C. in an atmosphere of hydrogen, then swaged and rolled at 900° C.

4. The Structures of the 92% Cold-Drawn Wires.

The 92% cold reduction in cross-sectional area resulted in wires with fibrous structures, which were revealed by etching in a dilute solution of potassium cyanide by means of an alternating current. This method of etching is preferred to attack by hot *aqua regia* or by molten salts containing sodium peroxide. The high corrosion-resistance of platinum increases the tendency to pitting during prolonged etching and makes it difficult to obtain the desired sharpness of detail in the photomicrographs.

Fig. 3 (Plate LXX) shows the fibrous structure of cold-drawn wire produced from a compact which had been sintered and rolled at 900° C. The 92% cold-drawn regular platinum wire also had a fibrous structure, similar to that illustrated in Fig. 3. X-ray diffraction patterns indicated that the orientation of the fibrous structure was independent of the method of production, the cube diagonal [1.1.1.] being parallel to the axis of the sintered or regular platinum wire.

5. Results of Annealing the 92% Cold-Drawn Platinum Wires.

(a) Microscopic and X-Ray Investigations.

Microscopic examination showed that regular platinum, from all batches, had undergone equi-axial recrystallization at a temperature

TABLE III.—The Temperature of Recrystallization of Cold-Drawn Sintered Platinum Wire.

Temperature of Sintering and Hot Working of Platinum Compact, ° C.	Temperature of Columnar Recrystallization of Cold-Drawn Platinum Wire, ° C.
900°	1200°
1100°	1100°
1400°	800°

below 700° C. after heating for 15 min. Under these conditions the sintered platinum showed no alteration, and only at higher temperatures was there a change from a fibrous to a columnar structure. The lower the temperature of sintering and hot working, the higher the temperature at which the columnar crystals appeared, as indicated in Table III.

Fig. 4 (Plate LXX) and Figs. 5-6 (Plate LXXI) illustrate the types of structures obtained after heating 92% cold-drawn wires at 1200° C. for 15 min. Fig. 4 shows the columnar structure of wire produced from a compact which had been sintered and rolled at 900° C. In the case of Fig. 5 the compact had been sintered and rolled at 1400° C. Fig. 6 shows the equi-axed structure of regular platinum after recrystallization. The columnar structure in Fig. 4 is comparatively stable and has been found to undergo little change during 24 hr. heating at 1700° C., with no sign of equi-axial recrystallization.

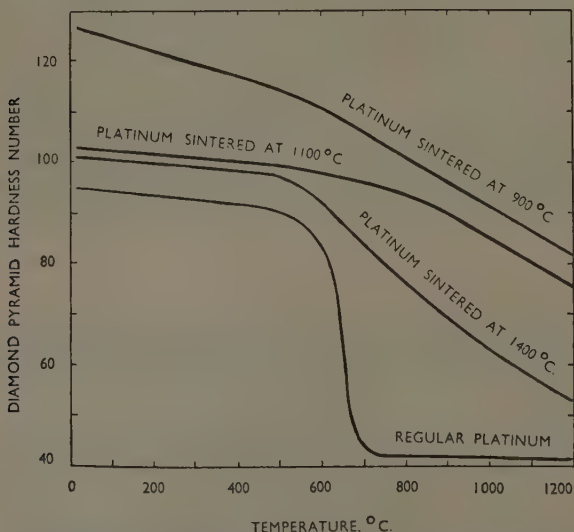


FIG. 12.—Effect of Heating for 15 min. on the Hardness Values (5 kg. load) of 92% Cold-Drawn Platinum Wires Produced Under Various Conditions.

X-ray investigations confirmed the results of the microscopic examinations. The change from a fibrous to a columnar or equi-axed structure was shown by the appearance of spotted rings, and it was found that a wire, made from a compact sintered at 900° C., after 18 hr. heating at 1200° C. gave a pattern similar to that of regular platinum which had been heated for 15 min. at 700° C.

(b) Hardness Determinations.

The effect of annealing on the hardness values of sintered and regular platinum wires is indicated by the curves in Fig. 12, the cold-drawn

wires being heated at the indicated temperature for 15 min. The regular platinum shows a rapid decrease in hardness at a temperature of approximately 650°C . The sintered platinum wires in the cold-drawn condition have higher hardness values than the regular platinum, and give

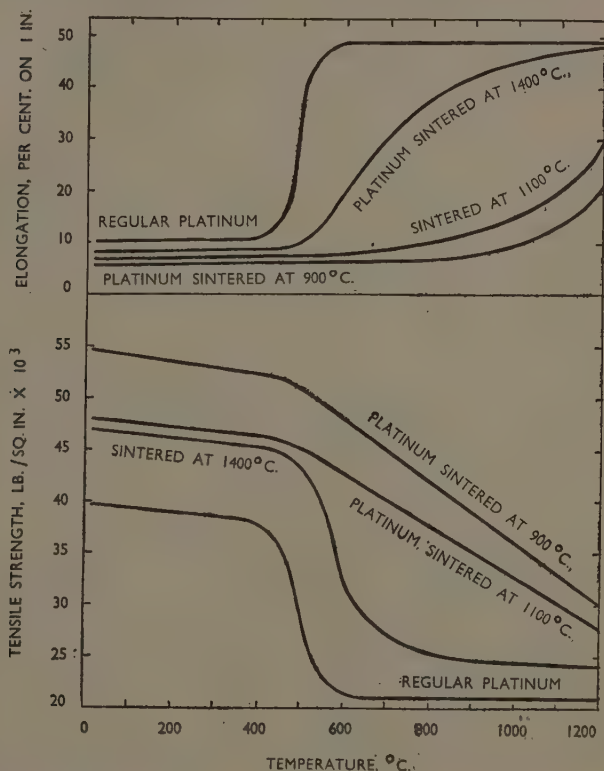


FIG. 13.—Effect of Heating for 15 min. on the Tensile Strength and Elongation of 92% Cold-Drawn Platinum Wires Produced Under Various Conditions.

lower rates of loss of hardness with increase in temperature, as compared with regular platinum. The lower the temperature of sintering and hot working, the greater the difference between the softening characteristics of sintered and regular platinum. After heating at 1200°C . for 18 hr., the sintered platinum wires had hardness values which were 10–20 D.P. units higher than the regular platinum wires.

(c) *Tensile Tests at Room Temperature.*

The effect of annealing on the tensile strength and elongation of sintered and regular platinum wires is illustrated by the curves in Fig. 13, the cold-drawn wires being heated at the indicated temperature for 15 min. The sintered platinum wires in the cold-drawn condition have greater tensile strengths than the regular platinum, and show lower rates of loss of tensile strength and lower rates of increase in elongation, with increase in temperature, as compared with regular platinum. These results are in accordance with the hardness values.

6. *Density Determinations.*

The densities of the 92% cold-drawn wires of 0.047 in. dia., were determined after cleaning and degreasing the wires in acetone. A length of each wire weighing about 25 g. was coiled into a 3-cm.-dia. helix, weighed in air, suspended from a 0.002-in.-dia. platinum wire and weighed in distilled water at a constant temperature of 22° C. with an accuracy of 0.1 mg. The calculated density was corrected for air buoyancy and for variation in water density from unity.

Cold-drawn wires produced from sintered and hot-worked platinum had lower densities than similar wires from regular platinum, and it was found that the density decreased as the temperature of sintering and hot working was lowered. This effect is shown in Table IV. Values of percentage volume porosity as calculated from the density, assuming regular platinum to have a max. density of 21.45 g./cm.³, are also given.

TABLE IV.—*The Porosity of Platinum Wires.*

Platinum Wire.	Temperature of Sintering and Hot Working of Platinum Compact, ° C.	Wire in 92% Cold-Drawn Condition.		Wire after Heating to 1200° C. for 15 min.	
		Density at 22° C., g./cm. ³	Volume Porosity, %.	Density at 22° C., g./cm. ³	Volume Porosity, %.
Sintered .	900°	21.307	0.67	21.112	1.58
” .	1100°	21.340	0.51	21.243	0.97
” .	1400°	21.352	0.46	21.327	0.57
Regular	21.446	0.02	21.443	0.03

Severe cold reduction by wire drawing had not eliminated all the porosity which was present after the hot working of the sintered powder compacts. The increase in porosity after heating the cold-drawn wires to 1200° C. was probably due to the expansion of gas in the pores of metal which was plastic at that temperature.

7. *Electrical-Resistance Measurements.*

Cold-drawn wires produced from sintered and hot-worked platinum had greater specific resistances than similar wires from regular platinum,

and it was found that a rise in the temperature of sintering and hot working was accompanied by a fall in the specific resistance (Table V).

TABLE V.—*The Electrical Resistance of Platinum Wires.*

Platinum Wire.	Temperature of Sintering and Hot Working, °C.	Wire in 92% Cold-Drawn Condition.			Ratio of Increase in Resistance to Volume Porosity.
		Specific Resistance, microhm-cm. at 0° C.	Increase in Specific Resistance of Sintered over Regular Platinum, %.	Volume Porosity, %.	
Sintered	900°	10.38	2.78	0.67	4.1
"	1100°	10.33	2.32	0.51	4.5
"	1400°	10.30	2.04	0.46	4.4
Regular	...	10.08

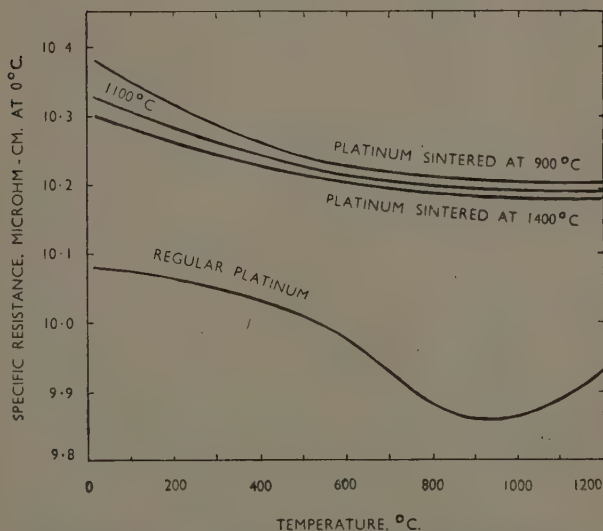


FIG. 14.—Effect of Heating for 15 min. on the Specific Resistance of 92% Cold-Drawn Platinum Wires Produced Under Various Conditions.

It will be seen that the increase in specific resistance of sintered platinum wires as compared with regular platinum is related to the amount of porosity which is present in the sintered platinum.

The effect produced on the specific resistance of the cold-drawn wires, by heating at various temperatures in air for 15 min., is shown in Fig. 14. In the case of regular platinum, the resistance decreased

owing to the removal of the strain-hardening, and then, above 900°C. , showed a slight increase. The wires produced from sintered platinum also showed decreases in resistance owing to the removal of strain-hardening, but at temperatures above 600°C. the decreases in resistance were comparatively small, so that after heating for 15 min. to 1200°C. the wires from sintered platinum had considerably higher specific resistances than wires from regular platinum.

8. Time-to-Rupture Tests.

These tests, made at 700°C. , proved that cold-drawn sintered platinum wire would sustain a greater load for a longer time, with less

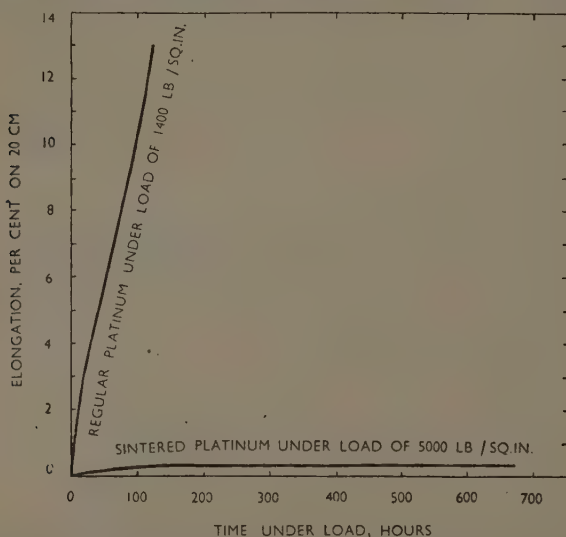


FIG. 15.—Time-to-Rupture Tests at 700°C. on 92% Cold-Drawn Platinum Wires Produced Under Various Conditions.

extension, than similarly cold-drawn regular platinum wire. The results of two tests, carried out under strictly comparable conditions, are shown graphically in Fig. 15. Cold-drawn regular platinum wire under a load of 1400 lb./in.^2 fractured after 120 hr., with an elongation of 13% on a length of 20 cm. Cold-drawn sintered platinum wire, from a compact which had been sintered and hot worked at 900°C. , fractured after 670 hr. under a load of 5000 lb./in.^2 , with an elongation of 0.35% on a length of 20 cm. Longitudinal sections of the wires,

adjacent to the points of fracture, are shown in Figs. 8-9 (Plate LXXII). The sintered platinum had retained a fibrous structure after 670 hr. under tensile stress, whereas the regular platinum had recrystallized and grain growth had occurred. Simple bend tests showed that both wires possessed high ductility after the long periods of heating.

9. High-Temperature Corrosion Tests.

On account of investigations which were being undertaken into aero-engine sparking plug electrode materials, the tests under this heading were concerned with platinum which had been strengthened by means of small additions of other metals which formed solid solutions with platinum, as for example, platinum with 4% tungsten. The high-temperature corrosion tests were used to give some indication of the behaviour of wires when tested under conditions simulating those in high duty aero-engine cylinders, namely, a high temperature, leaded fuel, a reducing atmosphere, and a bending stress. The combination of these factors results in attack of the wires by metallic lead, leading to grain boundary penetration, weakening, and embrittlement, with possible fracture of the wires under service stress. The test wires were produced from a mixture of platinum and tungsten powders, which was compacted, sintered until diffusion of the metals was complete, then hot worked as described under Section II. 1., and finally cold drawn to 0.02 in. dia. The regular alloy was produced by melting the constituent metals in a high-frequency furnace and the ingot worked to wire by a procedure similar to that used for the sintered alloy. The wires were uniformly coated with electrodeposited lead, supported horizontally, and loaded in the middle as shown in Fig. 7 (Plate LXXI), then heated in hydrogen or a reducing gas mixture at 700°-1000° C. For a 2-in. length of wire, on the basis of elastic theory, each gramme of load produced a skin tensile stress of 1400 lb./in.² on the under-side of the wire, and an equal stress in compression on the upper side. Sintered wire, which retained a fibrous structure, showed less deflection during the test under load than did regular wire which had recrystallized. At the completion of the test the wires were tested for embrittlement by means of a bend test and then examined microscopically for depth of penetration by lead. Figs. 10-11 (Plate LXXIII) show the effect of lead attack on sintered and regular wires tested under similar conditions. The sintered wire has retained the fibrous structure and the lead has penetrated half-way to the axis of the wire, causing embrittlement of that part but leaving a ductile core. The regular wire has recrystallized and the lead has fully penetrated the wire, causing complete embrittlement.

IV.—DISCUSSION OF RESULTS.

The experiments have shown that sintered and regular pure platinum, when in the form of cold-drawn wires with fibrous structures, differ in certain physical properties, the sintered platinum having higher hardness, tensile strength, and electrical resistance, associated with lower density, than the regular platinum. These differences were found to be more marked as the sintering and hot working operations were performed at a lower temperature. On annealing the cold-drawn wires the fibrous structure of the sintered platinum was found to be stable at temperatures well above the recrystallization temperature of the regular platinum, and when the sintered platinum did recrystallize it was not in the equi-axed form but with a columnar structure.

The differences between sintered and regular platinum cannot reasonably be connected with the small amounts of impurities which are present in both cases, or with variations in the distribution of these impurities. In the case of regular platinum the effect of melting at a temperature above 1774°C . in contact with a refractory material would tend to decrease the purity of the metal, as compared with sintered platinum which was not heated above a temperature of 900°C ., and this result might be expected to raise the temperature of recrystallization of the regular platinum above that of the sintered metal. On the other hand, when ammonium chloroplatinate is ignited to form platinum powder it might be possible for the impurities to be concentrated on the surface of the powder particles and thus form grain boundary films in the fibrous wire which might raise the temperature of recrystallization of the sintered platinum. To test this possibility a sample of the purest platinum powder was dissolved in pure *aqua regia*, the platinum precipitated as "black" by means of pure formic acid, then filtered, washed, dried, compacted, sintered, and worked to wire. This wire was found to have a raised temperature of recrystallization. Another sample of platinum powder was allowed to fall in a fine stream down a vertical alundum tube furnace maintained at a temperature of 1500°C . A slow stream of dry hydrogen was passed up the tube and the platinum powder was received in a flask through which the hydrogen was passed before entering the tube. Under these conditions it was possible for any surface films or oxides to be reduced and the foreign elements to alloy with the platinum before the operations of compacting and sintering were performed. The resulting cold-drawn wire was found to have a raised temperature of recrystallization.

In view of the results of the above experiments and the fact that the platinum powder compacts were processed in the solid state under conditions selected to minimize contamination of the platinum, it may be

assumed that the differences between sintered and regular platinum do not arise from variations in the amount, character, or distribution of the impurities present in the metal, but more probably from some other factor. It is suggested that suitably dispersed porosity may provide an explanation of the high recrystallization temperature of cold-drawn sintered platinum as compared with regular platinum.

The experimental results have indicated that the amount of porosity, calculated from the density, which may be effective in raising the temperature of recrystallization of pure platinum is less than 1% by volume. The actual dispersion of this porosity in the original cold-drawn wire is apparently very fine and has not been conclusively determined by microscopic investigations, but can be surmised by considering the sequence of operations by which the cold-drawn wire is produced from the powder compact. Microscopic examination has shown that the particle size of the platinum powder is of the order of a few microns in diameter, which is comparable with the particle size of metals obtained by the reduction of their oxides.¹¹ During the sintering of the platinum powder compact at 900° C. the volume porosity diminished from the original value of 35% to a value of 32%, and microscopic examination showed that large numbers of small pores were still present. The compressive action of hot swaging and rolling greatly diminishes the amount of porosity, but probably does not essentially alter the distribution of the porosity, which is not unlikely to follow the porosity pattern of the sintered compact. The pores would, however, tend to be elongated in the rolling direction, and this effect would be intensified by the severe cold reduction necessary for the production of a fibrous structure. A longitudinal section of a severely cold-drawn wire shows a structure consisting of extremely elongated fibres, and it is probable that the pores have been correspondingly extended and, being thus orientated in relation to the fibrous structure, may conceivably constitute a hindrance to equi-axial recrystallization while permitting the formation of a columnar type of crystal. The suggested effect of finely dispersed porosity would probably be valid whether the pores were vacuous or filled with gas or with an inert solid phase. That the presence of finely dispersed porosity may be an essential factor in the raising of the recrystallization temperature of platinum is indicated by the results of an experiment performed on part of an ingot of regular platinum which remained from previous experiments. The ingot was converted into filings which were cleaned with acid, pressed into a compact, sintered at 900° C., hot worked as previously described, and finally cold drawn to wire, which was found to have physical properties similar to regular platinum wire. The sintered wire had a density corresponding to a porosity of 0.4%, but this porosity, presumably due to a

coarse dispersion, was ineffective in raising the recrystallization temperature.

The applications in practice of a metal or alloy containing suitably dispersed porosity may be directed to cases where improved mechanical properties and resistance to deterioration at high temperatures may result from a raised temperature of recrystallization or from the hindering of structural changes which would otherwise occur at the service temperature. Examples are the elements of resistance-heated furnaces, electrodes for sparking plugs, thermocouples, valve electrodes, and excess-temperature fuses. In the case of aero-engine sparking-plug electrodes, made from platinum alloys, it has been found advantageous for the fibrous structure, originally present in the cold-drawn wire, to be retained during the service life of the electrodes, which operate at a relatively high temperature, in order to minimize the embrittlement produced by the intergranular penetration of lead from the fuel.^{12, 13}

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11. G. L. Miller, *Iron Steel Inst. Special Rep. No. 38*, 1947, 8.
12. British Patent No. 556,253.
13. British Patent No. 575,998.

OBSERVATIONS ON THE RECRYSTALLIZATION 1171

CHARACTERISTICS OF ALUMINIUM-MAG- NESIUM-MANGANESE ALLOYS.*

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SYNOPSIS.

The recrystallization characteristics of eleven binary and ternary alloys of commercial aluminium containing up to 1% magnesium and 1.25% manganese were investigated.

In all the alloys where the deformation was less than critical, the structure developed by subsequent annealing, in which a slow rate of heating was employed, was found from X-ray examination to be characteristic of material in the recovered state or condition. Critical deformation resulted in the development of the maximum grain-size in each individual alloy, but with further cold rolling the grain-size became progressively finer and, for any given reduction, was independent of the annealing temperature.

For aluminium and an alloy with 1% magnesium the minimum or critical reduction necessary to induce recrystallization on subsequent heating at 550° C. was less than 1%. Additions of manganese resulted in a progressive increase in this critical reduction, which in the alloy with 1.25% manganese was between 12 and 15%, depending upon the preceding rolling and annealing conditions. In the ternary alloys also, manganese had a more marked effect on the critical reduction than magnesium, and consequently the alloys of high manganese content were not subject to the development of very large grain-size. In the more heavily cold-worked material, the two elements had the reverse effect, and the aluminium-manganese alloy developed larger grain structures on annealing than the aluminium-magnesium alloy, while in the ternary alloys grain-size was influenced mainly by magnesium content.

I.—INTRODUCTION.

BINARY aluminium alloys with up to 7% or so of magnesium, or up to 1.25% of manganese, and ternary alloys, in which the magnesium content is generally much greater than the manganese content, constitute important commercial classes of non-heat-treatable alloys. A substantial amount of data on the properties of these materials is available, which indicates that the two elements magnesium and manganese, in small proportions, have very similar effects on the mechanical properties of aluminium.

It is generally appreciated, however, that these two elements differ

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substantially in their influence on recrystallization and grain growth, but the information available is insufficient to indicate clearly the precise effect of each element in either binary or ternary alloys.

The investigation described was concerned with the determination of the effects of small alloying additions of magnesium and manganese, separately and together, on the recrystallization characteristics of cold-worked aluminium sheet.

In all the materials studied the relationship between deformation and recrystallization on subsequent annealing showed characteristics similar to those described by Carpenter and Elam¹ in their work on the recrystallization of pure aluminium. Thus, on any given sheet sample, a minimum or critical deformation was necessary to induce recrystallization on subsequent annealing, and was associated with the development of a large grain-size; while as the deformation was increased, the grain-size progressively diminished. The observations made on the effect of other alloying additions, of variations in the method of preparation of the sheet, and of the final annealing temperature itself, on the magnitude of the critical deformation and the associated grain-size, formed perhaps the most significant part of the investigation, since with the heavier deformations these various factors had a relatively slight importance. In addition, some observations were made on the structural condition obtained by annealing the alloys after deforming by less than the critical amount.

In most of the materials the critical deformation was found to be small, and it was not, therefore, possible to obtain an accurate value from the examination of specimens annealed after imposing a series of progressively increasing rolling reductions. Stretching, carried out on tapered tensile test-pieces, was found to be a more suitable method, and provided a range of reductions within which accurate measurements could be made, ranging from about 0.5 to 20%; while a complementary range of reductions of from 17 to 72% was obtained by cold rolling. A complete picture of annealing characteristics over a range corresponding to reductions from 0 to 72% has thus been obtained by combining the results of stretching and rolling experiments.

II.—EXPERIMENTAL WORK.

1. *Materials.*

The materials investigated included commercial aluminium; binary alloys with 1.0% magnesium and 1.25% manganese, respectively; and ternary alloys with 0.25, 0.5, and 1.0% magnesium and 0.25, 0.5, and 1.25% manganese in all nine possible combinations. All the alloys

in the series contained, in addition to the major alloying elements, 0.3–0.4% iron, 0.15–0.25% silicon, and about 0.02% each of copper and titanium.

10-lb. ingots, of $1\frac{1}{2}$ in. thickness, of each alloy were hot rolled to 0.4 in., and cold rolled in a series of reductions with intermediate anneals to sheets of four gauges, 0.048, 0.057, 0.080, and 0.145 in., the final reduction being approximately 50% in each sequence. The sheets at each of these four gauges were annealed together at 500° C. and rolled to 0.040 in., yielding samples with four separate rolling reductions of 17, 30, 50, and 72%.

2. *Plan of Investigation.*

All experiments were carried out on the sheets of 0.040 in. thickness with the four separate final or ultimate rolling reductions of 17, 30, 50, and 72% already referred to. Isochronal annealing curves plotted in Figs. 18–19 record hardness values after annealing at 100° C. intervals from 100° to 500° C., and grain-size values of specimens annealed at 500° C. are given in Table III. Stretching experiments were carried out on tapered test-pieces cut from the four series of hard-rolled sheets and annealed at 500° C., so that Table III also indicates the grain-size values for the tapered specimens prior to stretching. After stretching to the point of fracture, the tapered test-pieces were given a final anneal at temperatures of 400°, 450°, 500°, and 550° C., and grain-size values were determined on each at various positions along the test-piece length. Typical examples of annealed, stretched, and re-annealed test-pieces are illustrated in Figs. 1–3 (Plate LXXIV) and 12–15 (Plate LXXVII); while typical curves showing grain-size distribution on those test-pieces prepared from the sheet subjected to an ultimate rolling reduction of 72% and annealed at 500° C. before stretching, are given in Figs. 16–17. Critical rolling reductions associated with the maxima on curves such as those illustrated in Figs. 16–17, and the corresponding grain-size values, are recorded in Tables I–II.

In addition to visual determinations of grain-size on the recrystallized portions of stretched and annealed test-pieces, the structures present were investigated by X-ray diffraction methods both in the recrystallized and non-recrystallized portions, and typical examples of the patterns obtained are reproduced in Figs. 4–7 (Plate LXXV) and 8–11 (Plate LXXVI). The recovered condition was shown to be present in the non-recrystallized areas adjacent to the critically deformed and recrystallized zones.

It will be evident that data obtained in stretching experiments are more comprehensive, and are correlated with a greater number of

processing stages than those obtained in the rolling experiments. This difference in procedure was deliberate, for the stretching experiments embraced the ranges in which critical reduction occurred, while the rolling experiments were concerned with the heavier reductions, which are of less importance to the investigation. Although rolling experiments preceded stretching experiments, in the description and discussion which follows the stretching experiments are dealt with first, since they are concerned with small deformations, i.e. from 0 to 20%, and the rolling experiments thereafter carry the results into a range of deformation from 17 to 72%.

By combining the results of stretching and rolling experiments, critical reductions and the corresponding grain-size values are obtained over a range of 0–72% and annealing temperatures of 250°–550° C. In plotting the curves reproduced in Figs. 20–21, the figures used are those from the columns of Tables I–II relating to stretching of material with an ultimate rolling reduction of 50%, since the rolling data, taken from Figs. 18–19 and Table III, were obtained on samples on which a reduction of 50% was applied prior to the final rolling.

3. *Annealing Procedure.*

For alloys which are substantially uniform solid solutions under all conditions of annealing, as are most of those in the present series, Eastwood, James, and Bell² found that varying the rate of heating had little effect on grain-size, which was determined mainly by the amount of deformation. Although results reported subsequently by Anderson and Mehl³ on rates of nucleation and grain growth in aluminium indicate that this conclusion may not be strictly correct, it seems clear that the rate-of-heating factor is of only secondary importance from the point of view of the present investigation.

Beck and his co-workers, in investigations on the annealing of aluminium–magnesium⁴ and aluminium–manganese⁵ alloys, have shown that with prolonged periods of heating, grain-size generally increases progressively, but careful consideration of their data indicates that most of the growth takes place in a period shorter than that used in the work now described, while thereafter very long periods are required for any substantial grain growth.

The present investigation was concerned with the initial recrystallization of cold-worked alloys, and only one heating procedure was employed; while this was rigidly standardized, it seems probable that the exact method of heating was of no great significance in determining the recrystallization behaviour or the grain-size values.

The procedure was to introduce the specimens, spread out in a single layer, into a forced air circulation furnace held at 250° C. Thereafter the furnace temperature was uniformly increased, by the use of an automatic, clock-driven, cam control, by 50° C./hr., and the maximum temperature was held for 15 min. before discharging the specimens.

4. Measurement on Stretched Test-Pieces.

Tapered test-pieces were machined from hard-rolled 0.040 in. sheet, with their longitudinal axes transverse to the final direction of cold rolling. They were 6 in. long, and tapered uniformly from 1 in. in width at the two ends to $\frac{1}{2}$ in. in width at the centre. Before stretching, the test-pieces were annealed at 500° C., and after stretching to fracture, the separate halves were re-annealed at temperatures of 400°, 450°, 500°, and 550° C.

For the correlation of grain-size with reduction in area, a series of parallel lines was scribed on the back of each tapered test-piece before stretching, at every 0.10 in. for a distance of 1.5 in. from the centre, width and thickness at each position being measured before and after stretching. Reduction in area was generally less than 1% at the two wider ends, and over most of the length was less than 5%, so that considerable accuracy of measurement was necessary in the short central zone near the neck, in which deformations covering the remaining range of about 5–25% occurred.

After annealing, the test-pieces were etched in a mixture consisting of 3 volumes concentrated nitric acid, 1 volume concentrated hydrochloric acid, and 1 volume water, to reveal the nature and extent of the recrystallized zone. The structure was examined by X-ray diffraction methods, the visible grain-pattern being used as a guide in selecting and identifying areas. X-ray examination was not confined to the recrystallized zone, but included various positions in the unrecrystallized zone, since the object was to identify the structural condition, i.e. recrystallized, recovered, or cold-worked. Grain-size evaluation in the recrystallized zones was carried out either under the microscope, making direct comparison with standard charts of $\times 100$ magnification, or, alternatively, by either low-power or direct visual comparison with the same charts, making adjustments of $\times 10$ or $\times 100$ to the measured values.

5. Rolling Procedure.

The rolling reductions were made in several small passes to avoid undue heating of the specimens, but otherwise the rolling procedure calls for no special comment. Reduction in thickness was measured

and etching of the specimens was carried out in the same manner as with the tapered test-pieces.

III.—DISCUSSION OF RESULTS.

1. *Stretching Experiments.*

Typical examples of the grain patterns obtained on stretched test-pieces after annealing and etching are reproduced in Figs. 1-3 (Plate LXXIV) which illustrate the recrystallization behaviour of aluminium and the two binary alloys. The zone of recrystallization varies from a narrow band at the extreme tip of the fractured test-piece, to one covering almost the whole length.

For any one alloy and condition of annealing, the minimum or critical deformation necessary to induce recrystallization is revealed by the sharp boundary to the recrystallized zone, and maximum grain-size is invariably found in the critically deformed zone adjacent to this boundary, while increased deformation beyond the critical amount results in a progressive diminution in grain-size.

(a) *X-Ray Diffraction Patterns.*

After locating the recrystallized zones of test-pieces by etching, X-ray examination was carried out at suitable positions along the length, and the diffraction patterns compared with the visually observed grain structures. The patterns obtained on aluminium and the 1.25%-manganese alloy re-annealed at 500° C. are illustrated in Figs. 4-7 (Plate LXXV) and 8-11 (Plate LXXVI). Figs. 4-5 indicate the structures at the recrystallized tips of the test-pieces. Estimates of grain-size values of 0.25 and 0.5 mm., respectively, were obtained from the patterns, confirming the results of visual examination. In the zone of critical reduction, the diffraction patterns were unsuitable for determination of grain-size, and the values quoted in Figs. 6-7 were obtained visually. Just outside the recrystallized zone, the patterns (Figs. 8-9) consisted of sharp rings similar to those which have been previously described by Cook and Richards⁶ as evidence of recovery or removal of lattice distortion. Fig. 8 also shows one or two spots, which indicate that the X-ray beam had partly impinged either on the recrystallized zone or on an isolated new grain outside the zone. The remaining patterns indicate the structural condition of the least deformed broad ends of the specimens, which in aluminium (Fig. 10), after a deformation of 0.5%, is again "recovered". The manganese alloy (Fig. 11), in which deformation was smaller, appeared to have suffered little if any lattice change on annealing. Similar results were obtained from the examination of other stretched and annealed specimens.

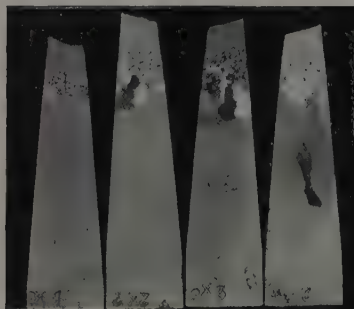
TABLE II.—Grain-Size (mm.) Corresponding to Critical Reduction on Stretched Test-Pieces.

Code No.	Composition, %	Final Annealing Temperature.												
		400° C.				450° C.				500° C.				
		Ultimate Rolling Reduction, %				Ultimate Rolling Reduction, %				Ultimate Rolling Reduction, %				
		17	30	50	72	17	30	50	72	17	30	50	72	
SRX	Commercial aluminium													
SRM	1.00	1.0	1.0	1.5	1.5	2.0	3.0	5.0	9.0	4.0	7.0	8.0	10.0	20.0
SRK	...	†	†	†	†	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.0	3.0
SRA	0.25	0.8	0.3	0.5	0.5	1.0	1.0	1.0	1.5	1.5	1.0	3.0	6.0	10.0
SRB	0.5	0.25	0.3	0.3	0.5	1.0	1.0	1.5	2.0	1.5	1.5	5.0	8.0	10.0
SRC	1.00	0.3	0.3	0.5	1.0	0.5	0.8	4.0	4.0	0.8	5.0	12.0	12.0	20.0
SRD	0.25	0.5	†	†	1.0	0.5	0.5	1.5	2.5	1.0	1.0	2.0	2.5	6.0
SRE	0.5	0.5	†	†	1.0	1.0	0.5	1.5	2.5	1.0	1.0	2.0	3.0	7.5
SRG	1.00	0.5	†	0.3	1.0	2.0	0.5	1.8	3.0	2.0	1.5	2.5	5.0	9.0
SRH	0.25	1.25	†	†	†	0.3	0.25	0.5	0.5	0.5	0.5	0.8	1.0	3.0
SRJ	0.5	1.25	†	†	†	0.3	0.25	0.5	0.5	0.5	0.5	0.8	1.0	3.0
SRK	1.00	1.25	†	†	†	0.5	0.25	0.5	0.5	0.5	0.5	1.0	1.5	4.0

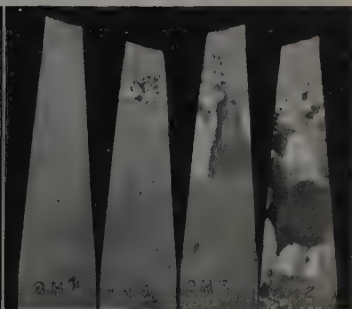
* Growth restricted by dimensions of test-piece.

† Grains too near tip for measurement.

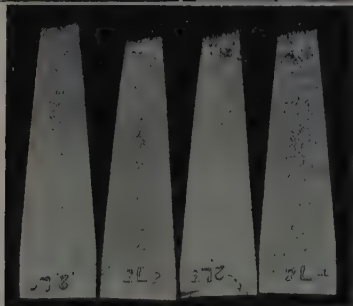
1
SRX



2
SRM



3
SRL



Figs. 1-3. Tapered Test-Pieces Cut from Sheet with Ultimate Rolling Reduction of 50%. $\times \frac{1}{2}$.

SRX Commercial-purity aluminium.

SRM 1.00%-magnesium alloy.

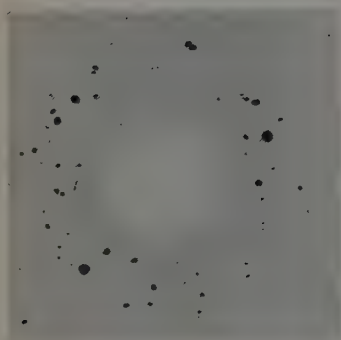
SRL 1.25%-manganese alloy.

Annealing temperature : before stretching 500° C.; after stretching (left to right) 400°, 450°, 500°, 550° C.

Grain-size values : before stretching (see Table III); typical grain-size plots after stretching and re-annealing (see Fig. 16).

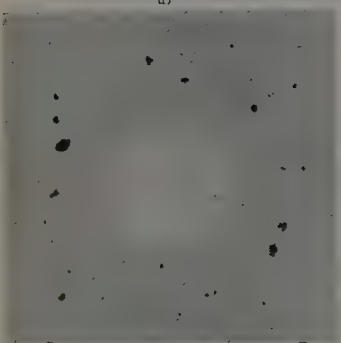
SKX Aluminium.

SKL 1.25%-Manganese Alloy.



4

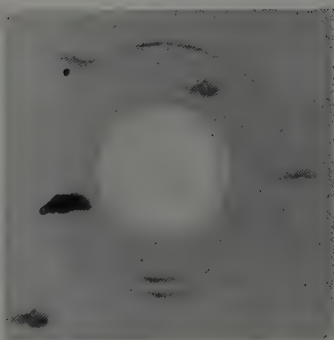
Tip



5

Grain-size : 0.25 mm.
Reduction in area : 13%.

Grain-size : 0.5 mm.
Reduction in area : 20%.

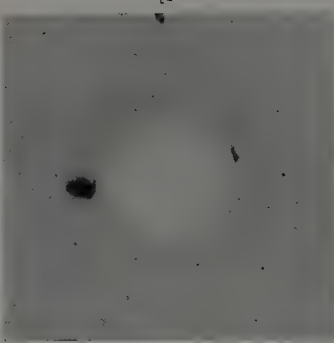


6

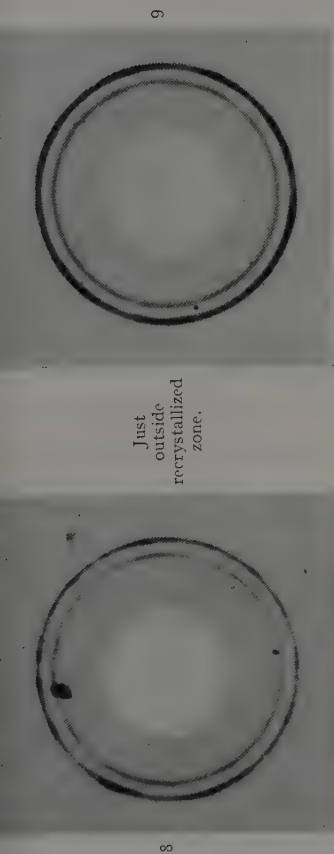
Zone of
critical
reduction.

Grain-size : 10 mm.
Reduction in area : 3%.

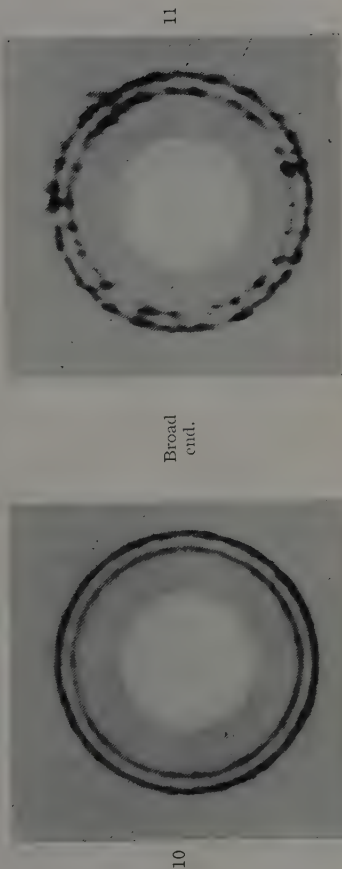
Grain-size : 1.0 mm.
Reduction in area : 13%.



7



Reduction in area : 2%.



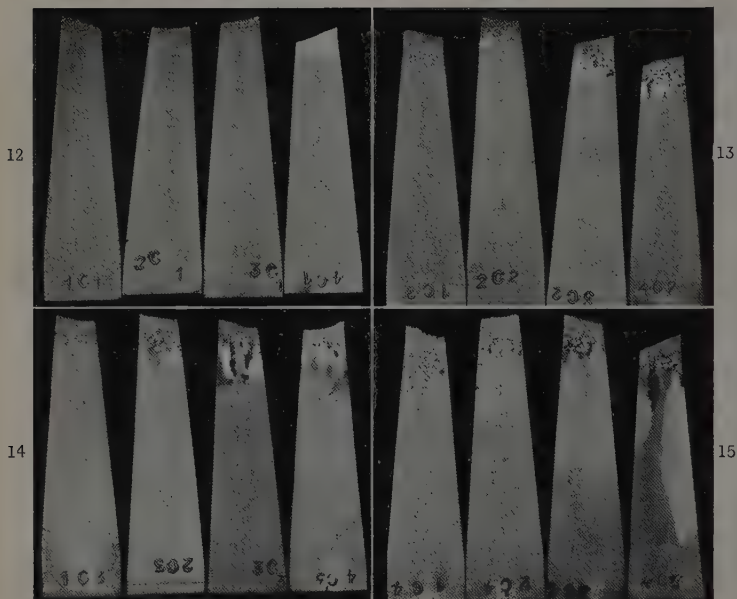
Grain-size (before stretching) : 0.12 mm.

Reduction in area : 0.1%.

Grain-size (before stretching) : 0.03 mm.

Reduction in area : 0.5%.

Figs. 4-11.—Typical X-Ray Diffraction Patterns on Specimens Reduced 72%, Annealed, Stretched, and Re-Annealed at 500° C.



FIGS. 12-15.—Tapered Test-Pieces of Alloy SRC (1.0% Mg, 0.25% Mn). $\times \frac{1}{2}$.
 Ultimate rolling reductions (left to right in each group of four): 17, 30, 50, 72%.
 Annealing temperature: before stretching 500° C.; after stretching (Fig. 12) 400° C., (Fig. 13) 450° C., (Fig. 14) 500° C., (Fig. 15) 550° C.
 Grain-size values: before stretching (see Table III); typical grain-size plots after stretching and re-annealing (see Fig. 17).

(b) Grain-Size Measurements in the Recrystallized Zone.

A typical set of stretched, annealed, and etched test-pieces of one individual alloy, on which measurements were made of the critical rolling reduction, and of the grain-size at various positions in the recrystallized zone, is shown in Figs. 12-15 (Plate LXXVII). Critical-reduction values for the whole series of alloys are recorded in Table I and the corresponding grain-size values in Table II.

TABLE III.—Grain-Size Values (mm.) on Rolled and Annealed Sheet.

Code No.	Composition, %		Ultimate Rolling Reduction, %			
	Mg	Mn	17	30	50	72
<i>SRX</i>	Commercial aluminium		0.042	0.04	0.035	0.031
<i>SRM</i>	1.00	...	0.04	0.035	0.031	0.028
<i>SRL</i>	...	1.25	1.5	0.3	0.15	0.12
<i>SRA</i>	0.25	0.25	0.8	0.08	0.06	0.05
<i>SRB</i>	0.5	0.25	0.25	0.06	0.06	0.05
<i>SRC</i>	1.00	0.25	0.05	0.031	0.026	0.023
<i>SRD</i>	0.25	0.5	0.6	0.2	0.08	0.07
<i>SRE</i>	0.5	0.5	0.6	0.08	0.07	0.06
<i>SRG</i>	1.00	0.5	1.5	0.035	0.033	0.026
<i>SRH</i>	0.25	1.25	0.4	0.17	0.14	0.12
<i>SRJ</i>	0.5	1.25	0.2	0.12	0.10	0.08
<i>SRK</i>	1.00	1.25	0.15	0.033	0.031	0.031

For aluminium, the critical reduction was less than 1% for a final annealing temperature of 550° C., irrespective of the magnitude of the previous rolling reduction, and the corresponding grain-size values were consequently large. For any given annealing temperature the addition of 1% magnesium was without appreciable effect on the critical reduction, but 1.25% manganese increased it substantially, especially at the lower temperatures and, after annealing at 400° C., recrystallization in the manganese alloy occurred so near to the test-piece tip that exact determinations of grain-size were impossible.

The results obtained on the ternary alloys showed similar features, and recrystallization behaviour was, except in the most highly alloyed specimens, typified by the results already referred to.

From the data given in Tables I-II, certain generalizations can be made which are applicable to all the alloys investigated. Thus, under any given conditions of final anneal, the smaller the ultimate rolling reduction, and therefore the larger the grain-size after the subsequent annealing operation, the larger was the critical reduction-in-

area observed in stretching, and the smaller the corresponding maximum grain-size on annealing after stretching. These differences in final grain-size after stretching obtained by varying the ultimate rolling reduction were, however, generally small, but tended to be most marked in pure aluminium *SRX*, and in alloys in which manganese was either absent or present in only a small proportion, i.e. in the binary alloy *SRM* and three ternary alloys, *SRA*, *SRB*, and *SRC*.

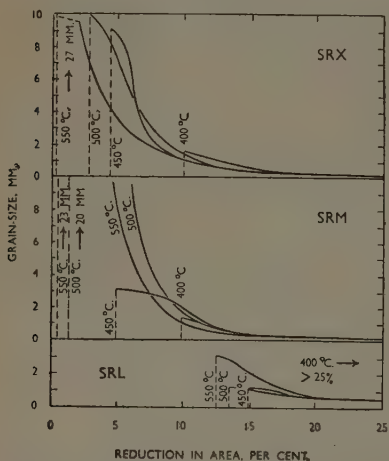


FIG. 16.—Grain-Size Values on Stretched Test-Pieces: Aluminium and Binary Alloys. Previous rolling reduction 72%.

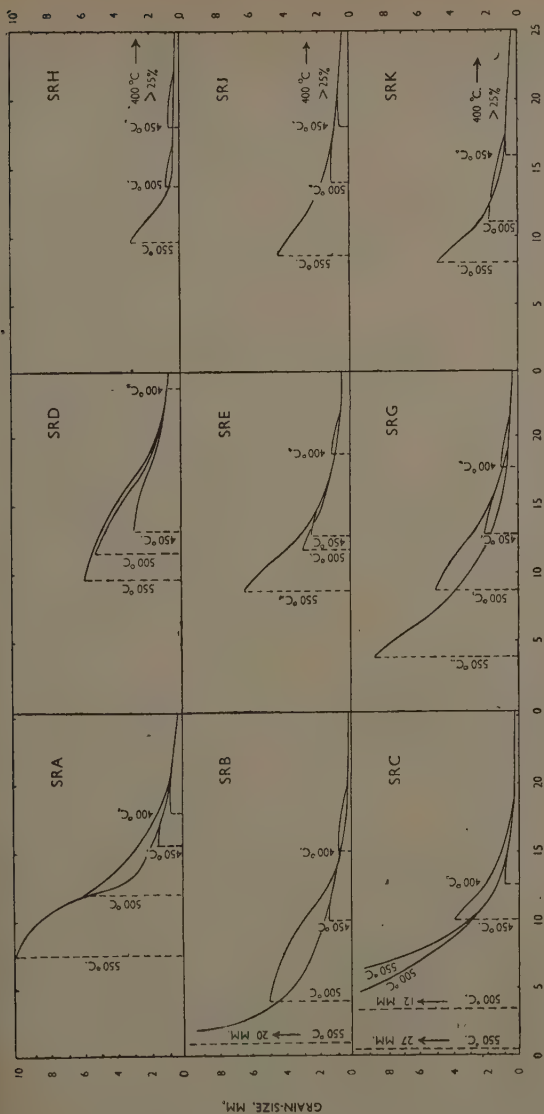
SRX Commercial aluminium.
SRM 1.0%-Mg alloy.
SRL 1.25%-Mn alloy.

are all, within the limits of experimental error in grain-size measurement, coincident. It is evident, therefore, that progressive raising of the annealing temperature had little effect on grain-size in the already recrystallized zone, but resulted in the further spread of recrystallization towards the broad, less deformed end of each test-piece, grain-size becoming progressively larger with each advance of the recrystallized-zone front. In other words, for any given reduction, the grain-size was unaffected by variations in the annealing temperature.

2. Rolling Experiments.

Annealing curves for aluminium and the binary alloys are shown in Fig. 18 and for the ternary alloys in Fig. 19. Most of the curves are of a

Typical curves, showing variation in grain-size with reduction-in-area in individual test-pieces, are plotted (Figs. 16-17) from measurements at positions along the test-piece length corresponding to 10, 15, and 20% and to the critical reduction. Only those curves relating to specimens with an ultimate rolling reduction of 72% are illustrated, and thus each curve represents the grain-size variation in one individual test-piece, but sheet prepared with other rolling reductions showed similar features. It will be noticed that the four separate curves for any one alloy annealed at a series of temperatures



REDUCTION IN AREA, PER CENT.

FIG. 17.—Grain-Size Values on Stretched Test-Pieces: Ternary Alloys. Previous rolling reduction 72%.

SRA 0.25% Mg, 0.25% Mn.
SRD 0.5% Mg, 0.5% Mn.
SRH 0.25% Mg, 1.25% Mn.
SRB 0.5% Mg, 0.25% Mn.
SRE 1.0% Mg, 0.5% Mn.
SRJ 0.0% Mg, 1.25% Mn.
SRC 1.0% Mg, 0.25% Mn.
SRG 1.0% Mg, 0.5% Mn.
SRK 1.0% Mg, 1.25% Mn.

simple form, that relating to aluminium with a rolling reduction of 50%, for example, is characterized by a shallow slope in the range 0°–200° C., followed by a steeper slope between 200° and 300° C., indicating the softening associated with recrystallization, while at high

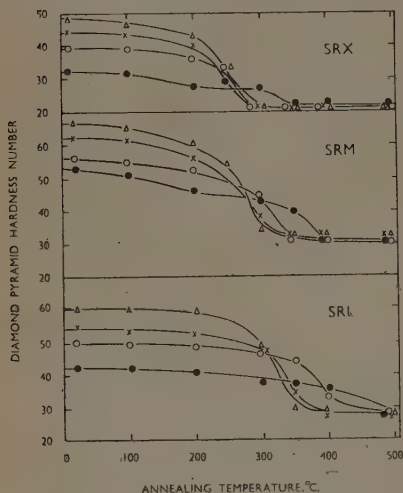


FIG. 18.—Annealing Curves of Aluminium and Binary Alloys.

SRX Commercial aluminium.
SRM 1.0% Mg alloy.
SRL 1.25% Mn alloy.

KEY TO FIGS. 18-19.

● Reduced 17% in thickness.
○ " 30% "
× " 50% "
△ " 72% "

obtained after annealing at this temperature are given in Table III. They show that manganese had the general effect of increasing grain-size, and magnesium of reducing it, the influence of either element being in proportion to the amount present. In any one alloy the grain-size was reduced progressively by increasing the rolling reduction.

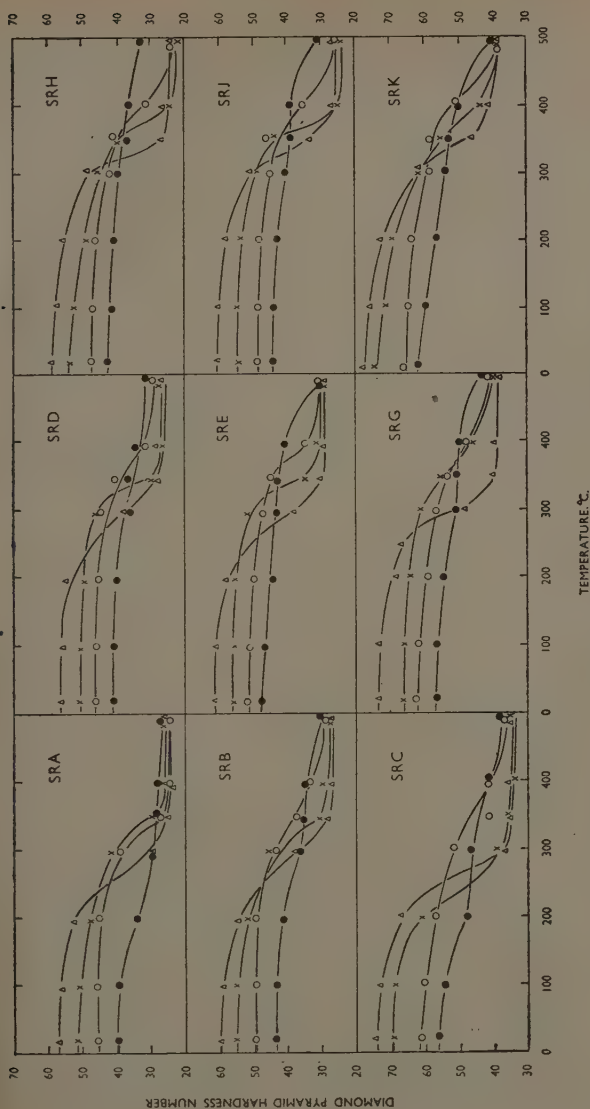
3. Combined Results of Rolling and Stretching Experiments.

(a) Annealing Temperature and Critical Reduction.

The methods by which critical-reduction values were obtained from stretched, annealed, and etched test-pieces have already been described

temperatures the curve is horizontal. Annealing curves for the alloys were generally of similar shapes, but magnesium in both binary and ternary alloys had the effect of rendering the break associated with recrystallization somewhat less sharply defined than that of pure aluminium, while in the ternary alloys it lowered the softening temperature. Manganese additions, on the other hand, resulted in more sharply defined recrystallization temperatures, which were raised progressively by increasing manganese.

The minimum annealing temperature at which all the alloys, with the complete range of rolling reductions, were fully recrystallized was 500° C., and the grain-size values



TEMPERATURE °C.

Fig. 19.—Annealing Curves of Ternary Alloys.

SRA 0.25% Mg, 0.25% Mn. SRD 0.25% Mg, 0.5% Mn. SRH 0.25% Mg, 1.25% Mn.
 SRB 0.5% Mg, 0.25% Mn. SRE 0.5% Mg, 0.5% Mn. SRJ 0.5% Mg, 1.25% Mn.
 SRC 1.0% Mg, 0.25% Mn. SRG 1.0% Mg, 0.5% Mn. SRK 1.0% Mg, 1.25% Mn.

and the results obtained recorded in Table I. From these values it is possible to plot curves, for reductions up to 25%, of critical reduction against annealing temperature. Data for reductions of greater magnitude must be obtained from the annealing curves for rolled material, and in order to derive values comparable with those obtained from stretching experiments, the rolling reductions applied to the alloy were regarded as the critical reductions corresponding to the temperatures at which maximum softening occurred. The validity of this derivation can be checked from the annealing curves for sheet reduced 17% in thickness by rolling. For example, the most highly alloyed material, *SRK*, softens at about 450° C. (Fig. 19), and comparison with Table I indicates that for *SRK*, subjected to the same earlier process as the rolled specimens, i.e. with a previous rolling reduction of 50%, and finally annealed at 450° C. after stretching, the critical reduction is 18%. Good agreement is obtained with those other alloys for which comparison is possible, and the final check is provided by the smooth character of the combined plots (Fig. 20) of the critical reduction values ranging up to a maximum of 72% for annealing temperatures from 250° to 550° C.

A study of the plots in Fig. 20 indicates that for all the alloys, the annealing temperature falls progressively with increase in cold work up to the maximum investigated of 72%, although the unalloyed aluminium appears to reach its minimum annealing temperature of 250° C. with less than 50% rolling reduction. The addition of 1.25% manganese raises the annealing temperature by 100°–150° C., depending upon the rolling reduction, while lesser additions have proportionate effects. On the other hand, magnesium has only a small effect on the annealing temperature in any of the alloys.

It is apparent that the curves are almost asymptotic to the horizontal as well as to the vertical axes, which suggests that for each alloy there is a minimum critical reduction. Alloys rolled with less than this minimum critical reduction would not, therefore, recrystallize, however high the annealing temperature. For aluminium, aluminium–magnesium, and the ternary alloys *SRB* and *SRC* which have high ratios of magnesium to manganese, this minimum is less than 1%, but it is raised progressively by further manganese additions, and all the alloys with 1.25% manganese require a minimum reduction of some 10% to induce recrystallization on annealing.

(b) *Grain-Size.*

The combined plots of grain-size values against reduction in area by rolling and stretching, for a final annealing temperature of 500° C.,

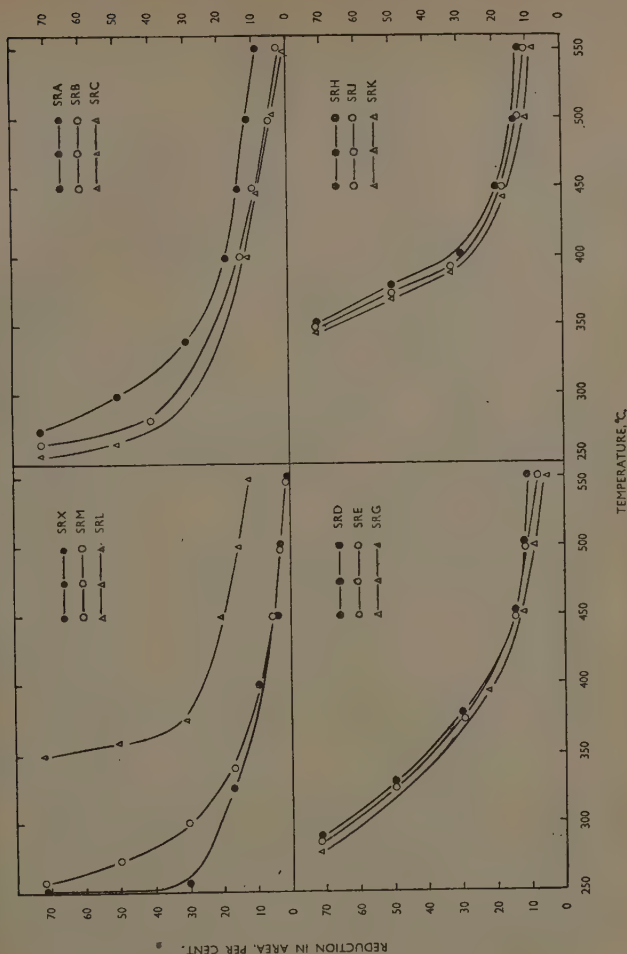


Fig. 20.—Critical Reduction Values from Rolling and Stretching Experiments.

are shown in Fig. 21. The grain-size values for the stretched alloy are taken from Table II, the reduction-in-area values against which they are plotted being found in the corresponding columns of Table I. Grain-size values for the rolled alloy are taken from Table III, and although the curves are derived from critical-reduction values for an annealing

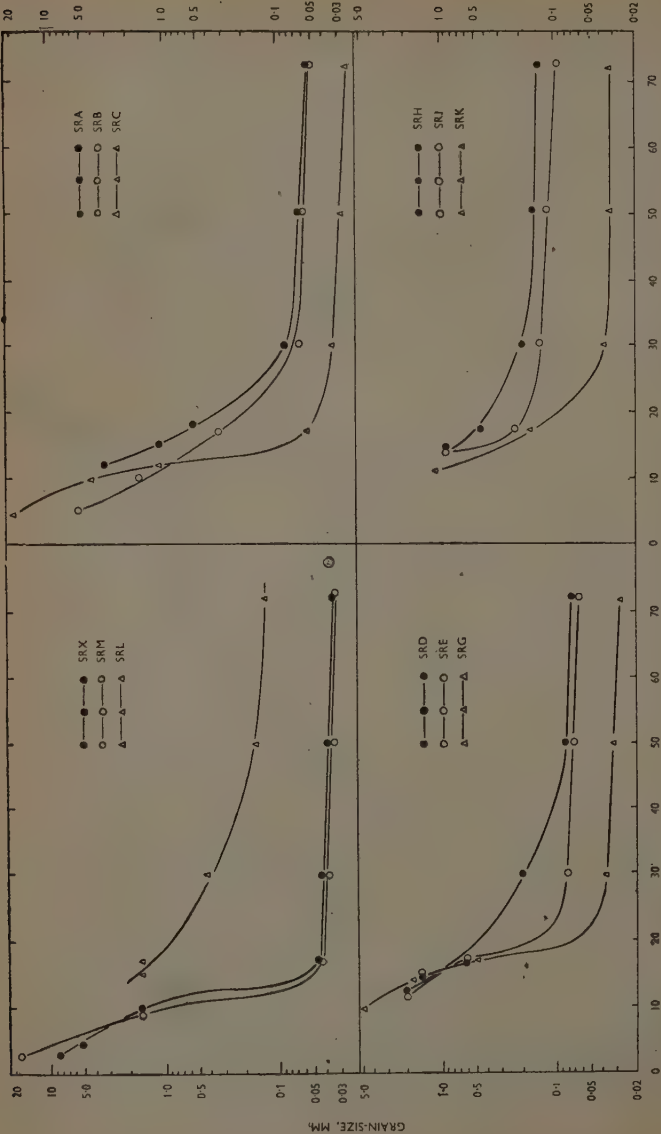


Fig. 21.—Grain-Size Values on Annealing at 500° C. after Rolling or Stretching.

temperature of 500° C., there is evidence available, as the plots in Figs. 16-17 indicate, to show that grain-size depends only on the prior treatment of the alloy and not on the annealing temperature. The curves in Fig. 21 may therefore be regarded as true for any annealing temperature and for reductions other than critical. Thus, if the annealing temperature were to be raised to 550° C., the curves would be unchanged except that they would extend somewhat further in the direction of smaller reduction-in-area values; while if the annealing temperature were reduced, they would be correspondingly shortened.

In pure aluminium and the 1% magnesium alloy, subjected to rolling reductions of more than 20%, grain-size is small and practically constant; with lighter deformations it increases steeply to a maximum value, which in the present experiments was probably restricted by the test-piece size and might otherwise have been very large indeed. There is no indication, however, in the shape of the curves reproduced in Fig. 21, that grain growth tends to be halted when mean grain diameter reaches a value equal to the test-piece thickness, as has been suggested by Beck and others.^{4, 5} The 1.25% manganese alloy shows a much smaller range of grain-size values, for the maximum is restricted by the large critical reduction, while with heavy reductions the curve shows an asymptotic approach to a value of about 0.1 mm. The ternary alloys all show the same characteristic features, large grain-size being developed by annealing after light deformation, each curve approaching asymptotically to a definite characteristic minimum grain-size value with increasing deformation.

With less than 20% deformation, all alloys develop large grains on annealing, and maximum grain-size tends to be restricted by manganese additions and to be increased by magnesium additions; manganese has the dominating effect except where the magnesium:manganese ratio is high.

With heavier rolling reductions the two alloying elements have the reverse effect, manganese tending to coarsen the grain, and magnesium to preserve the fine grain-size characteristic of unalloyed aluminium. Moreover, in each alloy a characteristic grain-size is developed, which cannot be refined further by increasing the reduction; neither element has an effect markedly stronger than that of the other in controlling grain-size where both are present in similar amounts. Thus alloys *SRA*, *SRB*, *SRD*, *SRE*, and *SRJ* are all intermediate in grain-size between *SRL* and *SRM* when annealed after a reduction of more than 50%. However, where magnesium is present to the extent of 1%, it exerts a dominating effect, and all the three ternary alloys with 1% magnesium, i.e. *SRC*, *SRG*, and *SRK*, have minimum grain-size

values of the order of 0.02–0.04 mm., i.e. about the same as the binary 1%-magnesium alloy *SRM*.

ACKNOWLEDGEMENTS.

The authors gratefully acknowledge the help and encouragement they have received from Dr. Maurice Cook, and the assistance of various colleagues in carrying out grain-size determinations and chemical analyses.

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THE EFFECT OF ROLLING AND ANNEALING 1172 PROCEDURES ON THE STRUCTURE AND GRAIN-SIZE OF ALUMINIUM-COPPER- MAGNESIUM ALLOY STRIP.*

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SYNOPSIS.

The effect of varying the last intermediate annealing procedure and the subsequent cold rolling on the structural condition after final heat-treatment at 500° C. of an aluminium-copper-magnesium alloy was investigated.

Where recrystallization occurred in the annealing operation, a large critical rolling reduction was always necessary to induce recrystallization on subsequent heat-treatment, and consequently the structures obtained were relatively fine-grained. In material quenched at the last annealing stage, critical rolling extended over a range of 10–20%, and the grain-size developed by the final heat-treatment was about 0.04 mm. In the slowly cooled alloy, however, the critical range extended from 8 to 12% and the grain-size obtained was about 0.07 mm., the changed value being probably the result of rejection of alloying constituents from solid solution prior to rolling. With heavier rolling reductions the rate of heating to the final heat-treatment temperature was found to be the only factor influencing grain-size.

In strip recrystallized after the last anneal and subjected to less than the critical reduction, heat-treatment resulted in the development of a condition which, from comparison of X-ray diffraction patterns with those previously obtained by Cook and Richards (*J. Inst. Metals*, 1948, 74, 583) in a similar alloy, was regarded as being recovered. Micro-examination of material in this condition revealed a grain pattern apparently identical with that of recrystallized material produced by an equivalent heat-treatment after 50% reduction, while mechanical properties and age-hardening characteristics were identical with those of recrystallized material of the same apparent grain-size. It is suggested that in recovered material each grain is an aggregate of mosaic units, differing insufficiently in orientation to affect light reflection from the surface, but differing sufficiently to result in a continuous diffraction pattern.

I.—INTRODUCTION.

IN commercial heat-treatable aluminium-copper-magnesium alloy strip, to which a final heat-treatment at 500° C. is normally applied,

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the grain-size varies but little and is seldom outside the range of about 0.025–0.05 mm. There are indications, however, that in the heat-treated alloy greater variations in structure may occur than those apparent from observations on grain-size only, and the matter has therefore been investigated in closer detail.

The work described in the present paper is concerned with the effect of varying the rolling and annealing procedures in the stages immediately preceding the final heat-treatment at 500° C., with the object of evaluating the effect of various combinations of treatments and rolling on the structural condition of the alloy and on the associated mechanical properties after final heat-treatment at that temperature. The thermal treatments were selected by reference to the annealing characteristics of the alloy, and special attention has been given to the further study of the recovered condition, evidence for the existence of which in this particular alloy was recently put forward in a paper by Cook and Richards.¹

II.—MATERIAL.

The composition of the alloy used was 4.26% copper, 0.79% magnesium, 0.63% manganese, 0.41% iron, 0.38% silicon, about 0.01% titanium, and less than 0.01% each of zinc and nickel. It was cast in the form of a 15-in.-dia. billet, which was extruded into a slab of 5 × 14 in. section. A portion of this slab was cross rolled hot to approximately 2 in. thickness, after which it was turned, rolled in the direction of extrusion down to the final hot-rolled thickness of 0.2 in., and finally annealed at 400° C. Subsequent cold rolling was carried out in the same direction as the final hot rolling.

III.—ANNEALING CHARACTERISTICS OF STRIP.

The 0.2 in. annealed stock was cold rolled to 0.104 in., and the normal annealing curve of this material, shown as the solid line in Fig. 1, was established by hardness tests on specimens heated for 90 min. in an air furnace and quenched. The principal features are similar to those of the curve described by Cook and Richards¹ for an alloy of the same type. There is a marked initial hardening, with maximum hardness at 160° C., followed by softening, which takes place in two well-defined stages. The first, which occurs between 160° and 300° C., is associated with lattice recovery, since X-ray diffraction patterns of the samples show an increase in definition without the appearance of discrete diffraction spots characteristic of the generation of new crystals. The second stage occurs in the range 320°–375° C. and is associated with

recrystallization; while the final increase in hardness, on heating at temperatures above that corresponding to minimum hardness, is attributed to the passing of copper and magnesium into solution.

Two additional curves are drawn as broken lines in Fig. 1, the upper one representing hardness values determined after 5 days' ageing at room temperature, and the lower one showing the result of annealing at 500° C., followed by cooling at a rate of 30° C./hr. to a series of lower

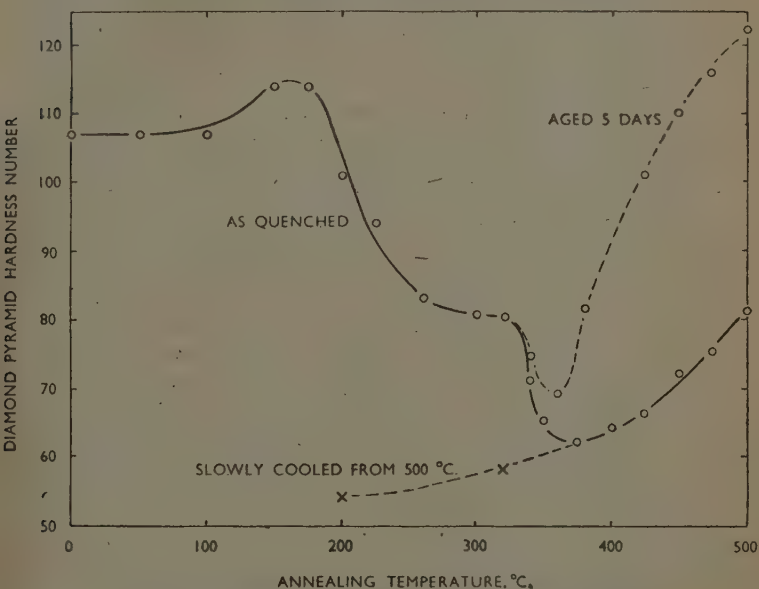


FIG. 1.—Annealing Curve of Strip After 50% Cold Rolling.

temperatures before quenching. This latter treatment is sometimes referred to as super-annealing, a treatment by which the alloy is prepared in the softest possible condition.

IV.—EXPERIMENTAL PROCEDURE.

1. Rolling and Annealing.

A number of experiments were designed to study the influence of variations in annealing conditions on the structure and grain-size after subsequent cold rolling and final solution heat-treatment. The latter is the normally accepted heat-treatment for the alloy, and consists in heating at 500° C. in an air furnace or salt bath for a definite period and

quenching in water. The term annealing has been applied to all thermal treatments prior to the final rolling reduction, even though some are actually equivalent to solution heat-treatment.

Samples of 0.2 in. annealed stock were cold rolled to 0.104 in. for the initial series of experiments, the results of which are summarized in Table I. Specimens in series *B1-B5* and *C1-C5* were annealed at 500° C., a temperature corresponding to that of normal solution heat-treatment, so that they were completely recrystallized. Annealing of *B1-B3* and *C1-C5* was carried out in an air furnace at a controlled slow rate of heating. The samples were placed in the furnace at 250° C., a temperature well below that of recrystallization for the material irrespective of its condition, and thereafter the temperature was raised at a constant rate of 200° C./hr., by a cam-actuated device, to the selected maximum temperature of 500° C., which was maintained for 15 min. *B1-B3* were quenched directly into water, while *C1-C5* were slowly cooled at 30° C./hr. to temperatures of 320°, 200°, or 50° C., as indicated in Table I, and quenched. *B4* and *B5* were annealed for half an hour at 500° C. in a salt bath and quenched.

Plunging into molten salt at 500° C. results in very rapid heating, especially with thin sheet, and direct measurements of rate of temperature rise are difficult to obtain. An approximate determination of the heating rate for sheet of 0.104 in. thickness was obtained by immersing a series of sheet samples of some low-melting-point metals, the thicknesses of which were adjusted to give equal thermal capacity per unit surface area, and measuring the time required for incipient melting. These observations indicated a rate of heating for 0.104 in. aluminium sheet, in the range 300°-400° C. in which recrystallization occurs, of 60° C./sec., which is about 1000 times the rate obtaining in the air furnace. For samples at the heat-treatment stage, which were thinner than 0.104 in., the ratio would be substantially greater than 1000.

Specimens in the series *B1-B5* and *C1-C5* were cold rolled, immediately after annealing, with a range of reductions in thickness from 0 to 75%, except that the procedure was varied for series *B2*, and the rolling was effected after the samples had age-hardened for 5 days at room temperature.

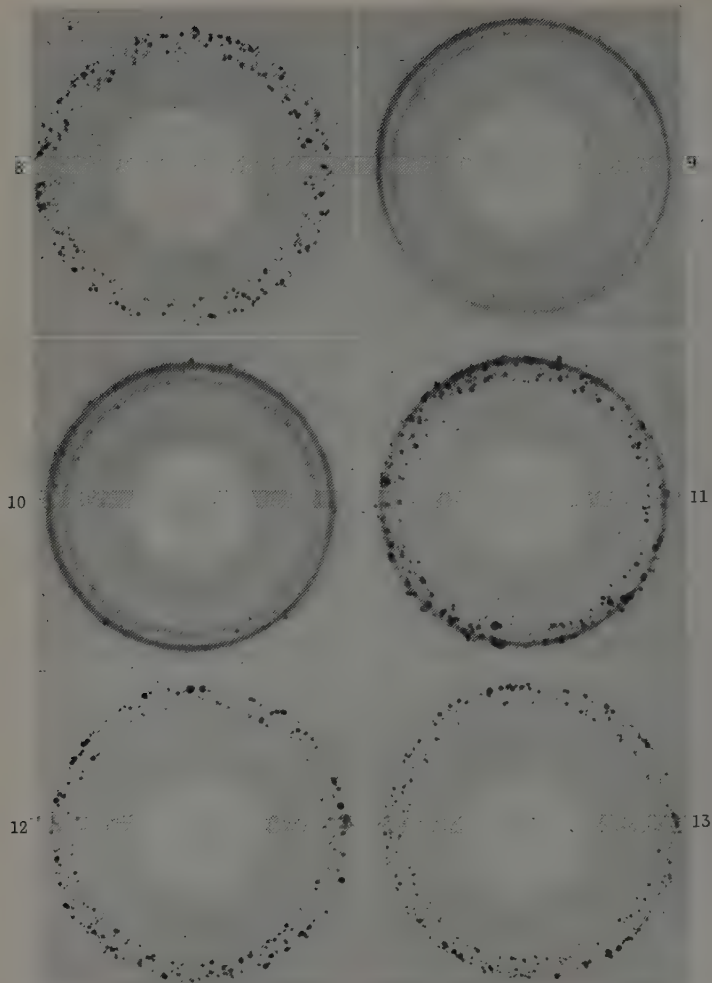
Strips of series *D1-D3* were initially annealed in an air furnace, using the controlled slow rate of heating, at a temperature of 375° C., which, by reference to the annealing curve in Fig. 1, corresponds to complete recrystallization with the minimum hardness that can be attained without slow cooling. *D1* was quenched after 15 min. at 375° C.; while *D2* and *D3* were slowly cooled at 30° C./hr. to 320° and 200° C., respectively, and quenched. Another strip, *E1*, was similarly



FIGS. 2-7.—Photomicrographs of Series B1, Annealed at 500° C., Quenched, Cold Rolled, and Heat-Treated at 500° C. $\times 100$.

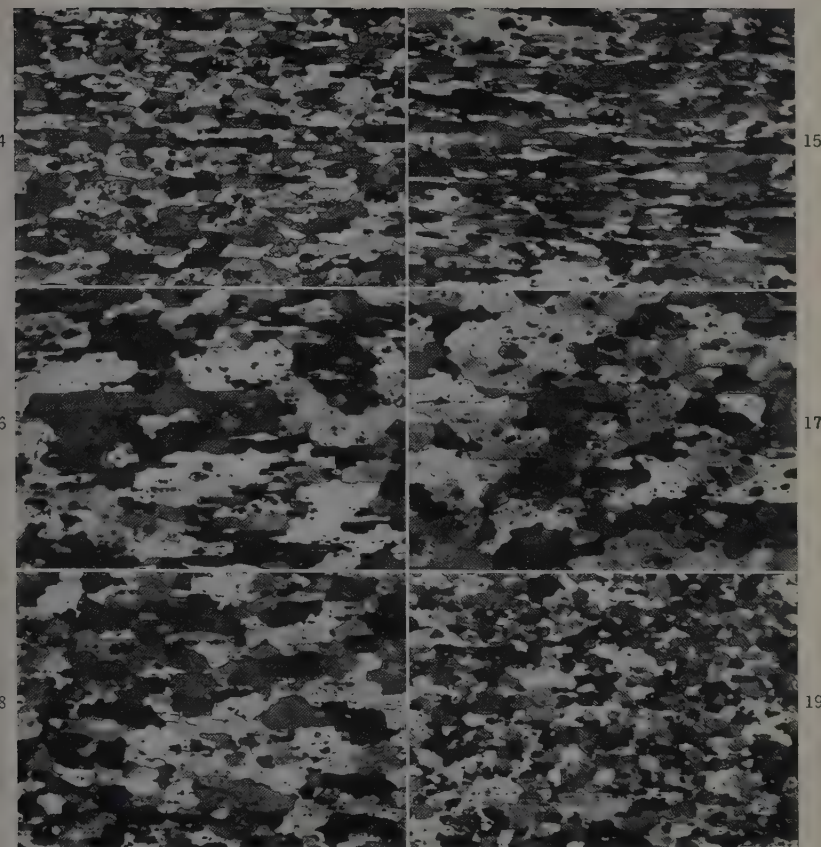
FIG. 2. Rolling reduction nil.
 " 4. " " 10%.
 " 6. " " 20%.

FIG. 3. Rolling reduction 5%.
 " 5. " " 16%.
 " 7. " " 30%.



FIGS. 8-13.—X-Ray Diffraction Patterns, Corresponding to Microstructures in Plate LXXVIII.

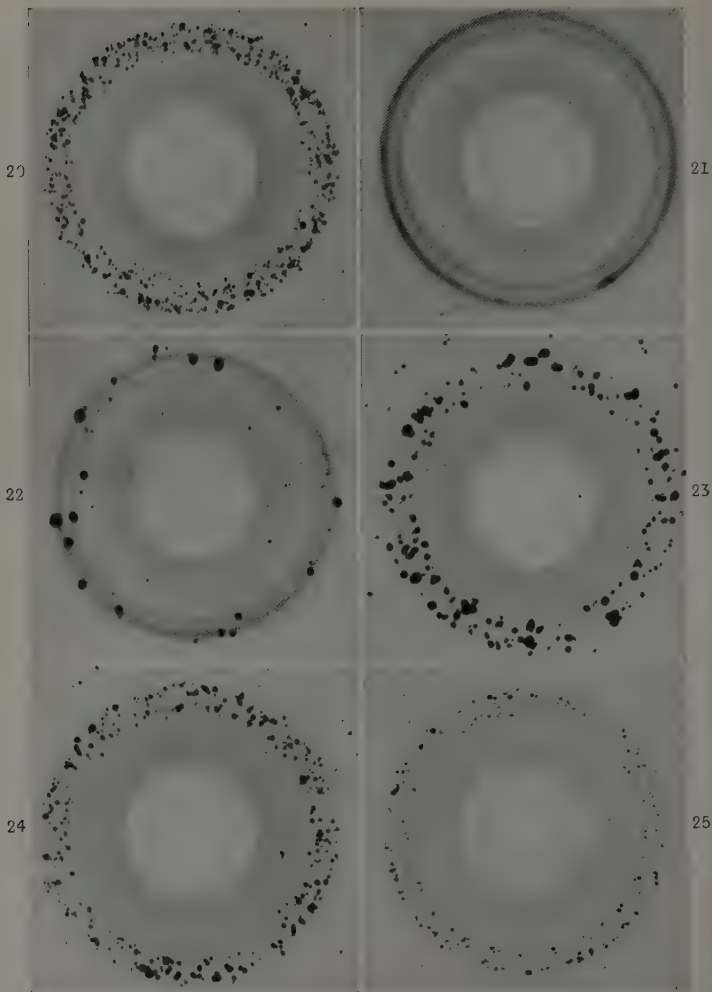
FIG. 8.	Rolling reduction	nil.	FIG. 9.	Rolling reduction	5%.
" 10.	"	10%.	" 11.	"	16%.
" 12.	"	20%.	" 13.	"	30%.



FIGS. 14-19.—Photomicrographs of Series C3, Annealed at 500° C., Slowly Cooled, Cold Rolled, and Heat-Treated at 500° C. $\times 100$.

FIG. 14. Rolling reduction nil.
 " 16. " " 10%.
 " 18. " " 20%.

FIG. 15. Rolling reduction 5%.
 " 17. " " 16%.
 " 19. " " 30%.



FIGS. 20-25.—X-Ray Diffraction Patterns, Corresponding to Microstructures in Plate LXXX.

FIG. 20.	Rolling reduction nil.	FIG. 21.	Rolling reduction 5%.
" 22.	" " 10%.	" 23.	" " 16%.
" 24.	" " 20%.	" 25.	" " 30%.

annealed in an air furnace at 320° C., so that it was in the fully recovered condition, that is, at minimum hardness without any recrystallization.

The final heat-treatment of the rolled samples was, as indicated in Table I, carried out either at the prescribed slow rate of heating in an air furnace or at a rapid rate in a salt bath, the specimens being quenched into water in both instances. The structure of the samples in each series was examined, and grain-size determined, both after the initial annealing treatment and after the final solution heat-treatment, the results of these observations being recorded in Table I.

A further series of experiments was carried out on samples *F1-F3* and *G1-G3*, prepared with special initial structures, the significance of which is discussed in a subsequent Section, and the observations are recorded in Table II.

2. Structural Examination.

Both micrographic and X-ray techniques were used to study the structural condition of the various specimens. For grain-size evaluation, the X-ray method was found to be more generally applicable, for it enabled recovered and recrystallized structures to be clearly differentiated, which was not possible with available techniques of micro-examination.

In the micrographic method the specimens were sectioned at right-angles to the surface in the direction of rolling, and examination was carried out on the central portions of the sections, where the grain-size was generally rather more uniform and consistent than at the surface. Estimations were made by comparison with a standard chart consisting of a series of photomicrographs (Figs. 26-33, Plates LXXXII and LXXXIII) of specimens with a range of grain-sizes on which very careful counts had been made of the number of grains/mm. in two directions on the etched section, one parallel to and the other normal to the surface. This chart was specially prepared for use in connection with the present investigation, since published grain-size charts which are available for the copper-base alloys and steels are unsuitable for use with the heat-treated aluminium-copper-magnesium alloys in which the form and distribution of grains is of a rather special character.

Prior to X-ray examination, in which unfiltered cobalt radiation was used, each specimen was deeply etched in caustic soda solution to remove the surface material. For grain-size evaluation, the Debye-Scherrer spot patterns were compared with standard patterns previously prepared from the series of specimens on which grain-size had been measured micrographically.

TABLE I.—*Effect of Annealing and Rolling Procedures on*
(Specimens cold rolled from 0.2

Series.	Anneal at 0.104 in.			Structure * and Grain- Size (mm.) After Annealing	Rolling
	Heating	Max. Temp., ° C.	Cooling		
B1	Air furnace	500°	Quenched	R 0.03	At once
B2	Air furnace	500°	Quenched	R 0.03	After ageing for 5 days at 20° C.
B3	Air furnace	500°	Quenched	R 0.04	At once
B4	Salt bath	500°	Quenched	R 0.02	At once
B5	Salt bath	500°	Quenched	R 0.025	At once
C1	Air furnace	500°	Slowly cooled to 320° C.	R 0.03	At once
C2	Air furnace	500°	Slowly cooled to 200° C.	R 0.03	At once
C3	Air furnace	500°	Slowly cooled to 50° C.	R 0.035	At once
C4	Air furnace	500°	Slowly cooled to 320° C.	R 0.04	At once
C5	Air furnace	500°	Slowly cooled to 200° C.	R 0.04	At once
D1	Air furnace	375°	Quenched	R 0.03	At once
D2	Air furnace	375°	Slowly cooled to 320° C.	R 0.03	At once
D3	Air furnace	375°	Slowly cooled to 200° C.	R 0.03	At once
E1	Air furnace	320°	Cooled in air	C	At once

TABLE II.—*Effect of Annealing and Rolling Procedures on*
(Specimens lightly rolled before

Series	Previous Treatment	Anneal at 0.104 in.			Structure * and Grain- Size (mm.) After Annealing
		Heating	Max. Temp., ° C.	Cooling	
F1	Annealed at 500° C. and quenched, followed by 8% rolling reduction.	Air furnace	500°	Quenched	C
F2		Air furnace	500°	Slowly cooled to 200° C.	C
F3		Air furnace	500°	Slowly cooled to 50° C.	C
G1	Annealed at 500° C. and slowly cooled to 50° C., followed by 15% rolling reduction.	Air furnace	500°	Quenched	R 0.07
G2		Air furnace	500°	Slowly cooled to 200° C.	R 0.07
G3		Air furnace	500°	Slowly cooled to 50° C.	R 0.07

* U = Unchanged by heat-treatment.

C = Recovered structure.

IR = Small proportion recrystallized (probably less than 10%).

Rolling and Annealing on Al-Cu-Mg Alloy Strip 633

Structures Obtained by Final Heat-Treatment at 500° C.
to 0.104 in. before annealing.)

Heat-Treatment (at 500° C.)	Structure* and Grain-Size (mm.)									
	Nominal Reduction in Thickness, %									
	0	2	5	10	14	16	20	30	50	75
Salt bath	U 0.03	C	C	IR	PR 0.04	PR 0.04	NR 0.03	R 0.03	R 0.02	...
Salt bath	U 0.03	C	C	IR	PR 0.04	PR 0.04	NR 0.035	R 0.03	R 0.02	...
Air furnace	U 0.04	C	C	C	PR 0.05	R 0.045	R 0.045	R 0.04	R 0.035	R 0.035
Salt bath	U 0.02	C	C	IR	IR 0.04	PR 0.04	NR 0.035	R 0.025	R 0.02	R 0.015
Air furnace	U 0.025	C	C	PR 0.055	R 0.045	R 0.045	R 0.04	R 0.04	R 0.035	R 0.03
Salt bath	U 0.03	C	C	PR 0.05	PR 0.045	R 0.04	R 0.04
Salt bath	U 0.03	C	C	PR 0.07	R 0.06	R 0.06	R 0.04	R 0.03	R 0.02	R 0.015
Salt bath	U 0.035	C	C	NR 0.065	R 0.06	R 0.06	R 0.045	R 0.03	R 0.02	...
Air furnace	U 0.04	C	C	PR 0.06	R 0.05	R 0.05	R 0.045	R 0.04	R 0.035	R 0.03
Air furnace	U 0.04	C	C	PR 0.07	R 0.06	R 0.06	R 0.06	R 0.05	R 0.035	R 0.035
Salt bath	U 0.03	C	C	IR	PR 0.045	R 0.045	R 0.04	R 0.03	R 0.02	R 0.015
Salt bath	U 0.03	C	IR	PR 0.06	R 0.06	R 0.05	R 0.04
Salt bath	U 0.03	C	C	IR	R 0.08	R 0.06	R 0.04	R 0.025	R 0.02	R 0.015
Salt bath	R 0.025	R 0.025	R 0.02	R 0.02	R 0.02	R 0.015	R 0.015

Structures Obtained by Final Heat-Treatment at 500° C.
annealing at 0.104 in.)

Rolling	Heat-Treatment (at 500° C.)	Structure* and Grain-Size (mm.)								
		Nominal Reduction in Thickness, %								
		0	2	5	10	14	16	20	30	50
At once	Salt bath	C	C	IR	PR 0.03	PR 0.025	NR 0.025	R 0.025	R 0.02	R 0.02
At once	Salt bath	C	C	IR	PR 0.06	R 0.05	R 0.04	R 0.025	R 0.02	R 0.015
At once	Salt bath	C	C	IR	R 0.07	R 0.07	R 0.05	R 0.04	R 0.025	R 0.02
At once	Salt bath	U 0.07	C	C	IR	IR 0.03	PR 0.025	NR 0.025	R 0.025	R 0.02
At once	Salt bath	U 0.07	C	C	NR	PR 0.07	R 0.05	R 0.04	R 0.025	R 0.02
At once	Salt bath	U 0.07	C	C	PR 0.08	PR 0.07	R 0.07	R 0.045	R 0.03	R 0.015

* PR = Large proportion recrystallized.

NR = Almost completely recrystallized (probably more than 90%).

R = Completely recrystallized.

V.—DISCUSSION OF RESULTS.

1. *Structure at the Annealing Stage and After Final Heat-Treatment.*

The recrystallization of commercial Duralumin subjected to a series of rolling reductions and finally heat-treated at 510° C. has been investigated by Eastwood, James, and Bell.² After rolling reductions of 2 or 5%, no recrystallization was observed, but after a reduction of 10%, a recrystallized structure of large grain-size resulted on heat-treatment; while after further rolling the grain-size became progressively finer. These observations did not appear to be altogether in accordance with ordinary commercial experience, but the investigators employed a rather special method of preparation, in which all specimens were slowly cooled after annealing and prior to rolling, in order to obtain the softest possible condition. Since this procedure appeared to have some possible significance, the cooling after annealing was varied in the present experiments.

The term "critical reduction" was adopted by Carpenter and Robertson,³ who have summarized investigations on the recrystallization of pure metals. In general, when annealed and fully softened metal is cold worked and re-annealed, no recrystallization occurs if the reduction is small. A definite and characteristic strain is required to induce recrystallization, and this minimum, or critical, reduction generally results in a very large grain-size on annealing, while as the amount of deformation increases, so the grain-size diminishes. In the present investigation the minimum reduction necessary for recrystallization was carefully determined for each sample by the close spacing of rolling reductions in the appropriate range. The term critical reduction has been used to describe this minimum reduction, for although, for reasons which became apparent in the investigation, no very large grains were obtained, it seemed clear that the general behaviour was comparable with that described by Carpenter and Robertson on other materials. The relationship is more clearly brought out in an earlier paper,⁴ in which other aluminium alloys, showing a wider range of critical reductions, were investigated.

In the experiments reported in Table I, the structural condition was determined both in the annealed condition and after heat-treatment. After annealing the structure was, except in series *E1*, fine-grained and fully recrystallized. Grain-size at the annealing stage appeared to be independent of maximum temperature, provided this was sufficiently high to cause recrystallization. Rapid heating in the salt bath resulted, however, in a somewhat finer grain-size than slow

FIGS. 26-33.—Chart of Grain-Size Standards for Aluminium-Copper-Magnesium Alloy Sheet.

L = Mean grain diameter in rolling direction.

T = Mean grain diameter perpendicular to sheet surface.

G.S. = Grain-size, $\sqrt{L \times T}$

Paper by Chadwick, Richards, and Sumner, *Journal of the Institute of Metals*, 1949, **75**, 627.

mm.
 $L = 0.03$
 $T = 0.017$
 $G.S. = 0.023$

$L = 0.043$
 $T = 0.022$
 $G.S. = 0.031$

27

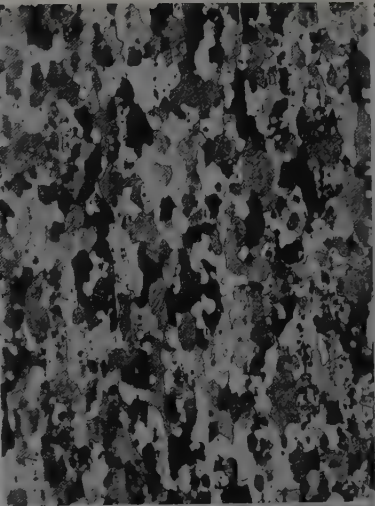


26



mm.
 $L = 0.023$
 $T = 0.013$
 $G.S. = 0.017$

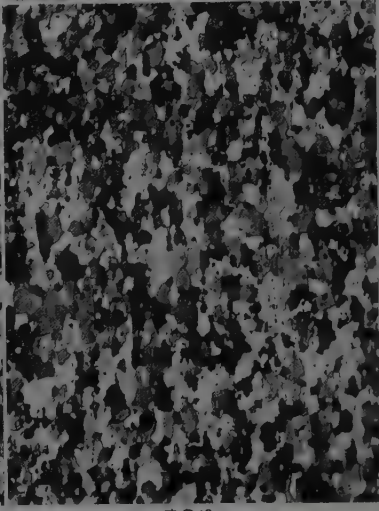
$L = 0.034$
 $T = 0.020$
 $G.S. = 0.026$



× 100.

29

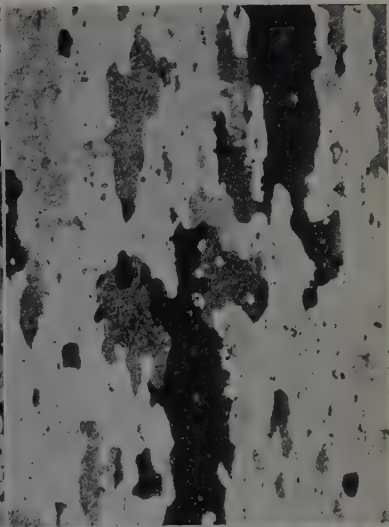
28



mm.
L = 0.085
T = 0.038
G.S. = 0.057

L = 0.19
T = 0.074
G.S. = 0.12

31

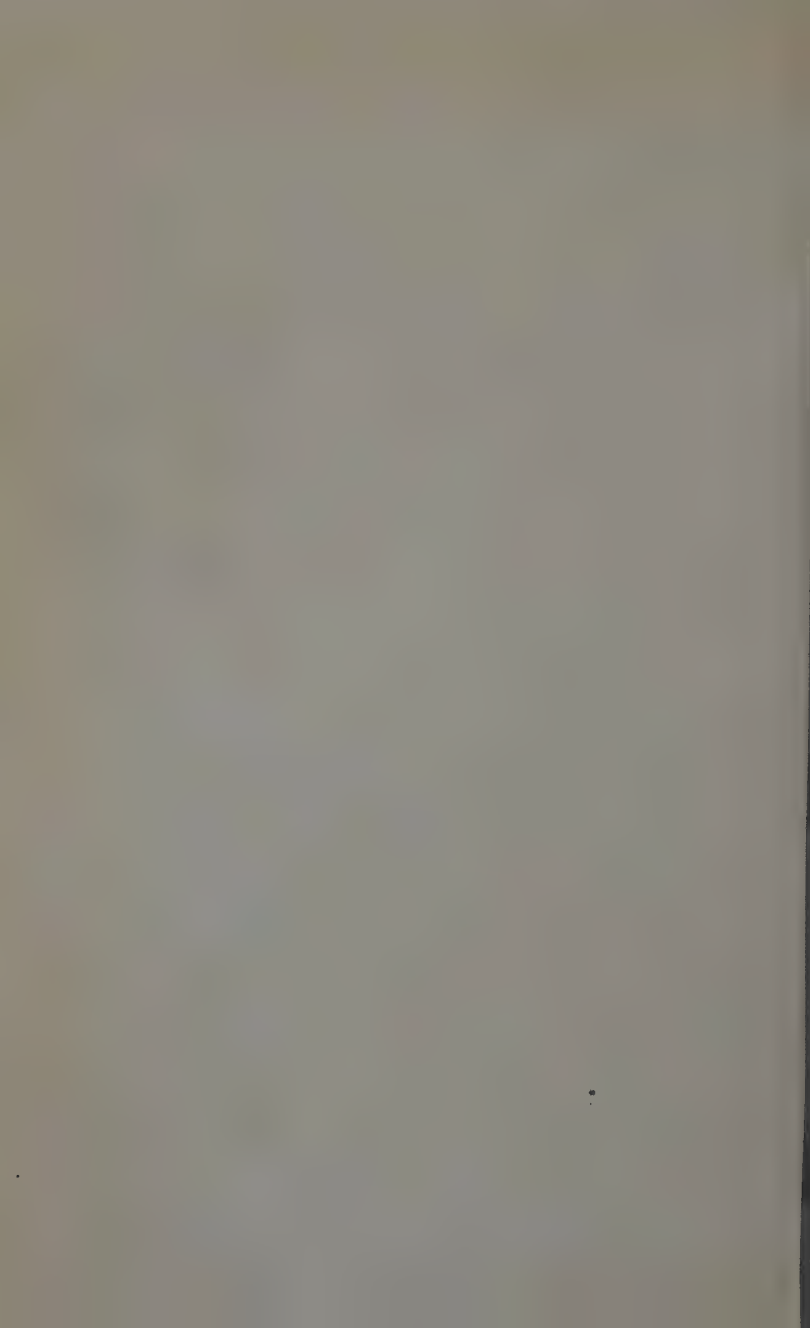


30



mm.
L = 0.059
T = 0.030
G.S. = 0.042

L = 0.11
T = 0.055
G.S. = 0.077



heating in air, but the ratio of mean grain-diameters obtained by the two methods of annealing was less than 2:1. Annealing at 320° C. (series *E1*) resulted in a recovered structure with a Debye-Scherrer pattern consisting of sharply defined rings of uniform intensity.

Observations on the structure after final heat-treatment relate mainly to experiments in which both rolling and heat-treatment were carried out immediately after annealing, but they also include one series, *B2*, in which full room-temperature age-hardening had occurred before rolling. This variation, however, had no effect on subsequent behaviour.

Examples of the microstructure and X-ray diffraction patterns obtained in typical series, *B1* and *C3* (Table I), in which recrystallization occurred at the annealing stage, are reproduced in Figs. 2-25 (Plates LXXVIII-LXXXI). After heat-treatment without intermediate rolling the structure was unchanged (Figs. 2, 8, 14, and 20). After a rolling reduction of 5% in thickness, the microstructures still appeared unchanged (Figs. 3 and 15), but the diffraction patterns (Figs. 9 and 21) consisted of sharply defined rings, identical in appearance with those obtained by Cook and Richards¹ as a result of annealing more heavily cold-worked material below the recrystallization temperature.

In any one series, maximum grain-size was observed in samples rolled with the critical reduction, the magnitude of which was influenced mainly by the method of cooling after the previous anneal. Thus, where quenching was employed, as in series *B1*, partial recrystallization occurred in the subsequent heat-treatment after a 10% reduction, as indicated by the spots present in the diffraction pattern (Fig. 10), but more than 20% reduction was necessary to secure complete recrystallization.

When, however, the alloy was slowly cooled, the critical reduction was smaller and more sharply defined. Thus, in series *C3*, recrystallization commenced at about 8% and was complete after about 12% rolling reduction; moreover, within the critical rolling range, the recrystallized grain-size for any given rolling reduction was considerably larger than in series *B1*, as can be seen by comparison either of diffraction patterns (Figs. 22 and 23) or of microstructures (Figs. 16 and 17) with corresponding members of the *B1* series (Figs. 10 and 11 and Figs. 4 and 5, respectively). Within the critical range grain-size appeared to be unaffected by the method of heating to the final heat-treatment temperature.

By increasing the rolling reduction, the grain-size developed by final heat-treatment became progressively smaller in all series, and for rolling reductions of 50 and 75%, the only factor which appeared to

have any significant influence on grain-size was the rate of heating in the final heat-treatment. Thus, as previously observed at the annealing stage, rapid heating in the salt bath reduced the mean grain-diameter to about half that obtained by the controlled slow rate of heating in the air furnace.

In series *E1* the grain-size, after any given rolling reduction, was very much smaller than in specimens rolled by a corresponding amount after full recrystallization. Comparison of actual grain-size values with those obtained for other series seemed to indicate that, prior to rolling, *E1* could be regarded as having a residual rolling reduction of about 50%. Thus the recrystallization behaviour of the alloy would seem to depend on the total reductions imposed before and after the recovery anneal.

In the experiments reported in Table I the structure after annealing was, apart from series *E1*, fine-grained and fully recrystallized. In further experiments, reported in Table II, earlier processing conditions were varied to give other types of structure at this stage. Thus, in series *F1-F3*, quenching followed by a small rolling reduction resulted in the development of a typical recovered structure on annealing at 500° C.; while in series *G1-G3*, by slow cooling and then giving a small rolling reduction, a recrystallized structure with a grain-size of 0.07 mm. was obtained. The subsequent experimental procedure was similar to that previously described; annealing was followed by quenching or slow cooling, and a series of rolling reductions was imposed followed by heat-treatment.

In series *F1-F3*, in which the annealing temperature was such that the recovered condition was obtained, a smaller reduction sufficed to bring about recrystallization in the subsequent heat-treatment than in the corresponding series, *B1*, *C2*, and *C3*. It would seem, therefore, that, as in series *E1*, rolling reductions before and after the recovery anneal were in a sense additive in their effect on subsequent recrystallization behaviour.

In the series *G1-G3* the finally heat-treated specimens showed no systematic difference in grain-size from the corresponding members of the *B1*, *C2*, and *C3* series, but there was some indication that, as a result of the coarse-grain structure at the annealing stage, the critical rolling reduction was slightly increased.

2. Effect of Structure on Mechanical Properties After Quenching from 500° C.

Aluminium-copper-magnesium alloys of the type under investigation are normally used in the heat-treated condition, obtained by quench-

ing from a temperature of about 500° C., and mechanical properties can be most usefully compared either immediately after quenching or after age-hardening at room temperature for several days. In the present investigation specimens were prepared in which annealing and rolling schedules were so arranged as to obtain two widely different grain-sizes on heat-treatment at 500° C. In addition, by imposing small rolling reductions on each of these specimens and re-heat-treating at 500° C., further samples were produced, which, on X-ray examination, showed diffraction patterns characteristic of the recovered condition, although, on metallographic examination, grain-sizes were apparently equal to those of the original recrystallized specimens.

Mechanical properties determined immediately after quenching, after 5 days, and after 28 days, are indicated in Table III. The values are the mean of six determinations, three of which were carried out on

TABLE III.—*Mechanical Properties of Sheet in Differing Structural Conditions.*

Structure and State When Tested.	0.1% Proof Stress, tons/in. ²	Ultimate Tensile Strength, tons/in. ²	Elongation, % on 2 in.
<i>Recrystallized : Fine grain</i> (mean grain-size 0.025 mm.)			
Within 15 min. of heat-treatment	8.1	20.0	22
Aged for 5 days at 20° C.	16.4	27.3	22
Aged for 28 days at 20° C.	16.3	27.3	22
<i>Recovered</i> (apparent grain-size by micro-graphic examination 0.025 mm.)			
Within 15 min. of heat-treatment	8.3	19.5	21
Aged for 5 days at 20° C.	16.3	26.9	22
Aged for 28 days at 20° C.	16.7	27.1	22
<i>Recrystallized : Coarse grain</i> (mean grain-size 0.05 mm.)			
Within 15 min. of heat-treatment	6.9	20.5	23
Aged for 5 days at 20° C.	15.1	27.0	21
Aged for 28 days at 20° C.	16.1	27.5	21
<i>Recovered</i> (apparent grain-size by micro-graphic examination 0.05 mm.)			
Within 15 min. of heat-treatment	7.2	20.0	21
Aged for 5 days at 20° C.	15.7	27.0	22
Aged for 28 days at 20° C.	16.2	27.4	21

test-pieces cut with their major axes in the rolling direction and three on test-pieces cut transversely. Of the recrystallized materials, the coarse-grained had lower proof-stress values than the fine-grained both in the quenched condition and after 5 days' ageing, but after the full

28-day period the difference was very much reduced. Ultimate tensile strength values, which are probably affected by strain-ageing during testing, showed, as would be expected, less marked differences. The recovered materials possessed mechanical properties at all three stages of ageing virtually identical with those of recrystallized materials of equivalent grain-size from which they were prepared.

VI.—THEORETICAL CONSIDERATIONS.

The experimental work described indicates that when the alloy is annealed, rolled, and fully heat-treated, recrystallization only occurs provided that a minimum or critical rolling reduction has been imposed, and its behaviour is thus comparable with that of pure metals referred to by Carpenter and Robertson.³ Grain-size is found to depend on various factors, including the previous annealing procedure, the rolling reduction, and the final heat-treatment conditions. Certain theoretical points arise in connection with the recrystallization behaviour observed, and these are discussed in Sub-Section 1. below. Where the alloy is rolled by less than the critical amount the recovered condition is developed by final heat-treatment, and the significance of observations on material in this condition and on its behaviour when subjected to further rolling and annealing treatments is discussed in Sub-Section 2.

1. *Factors Determining Grain-Size of Recrystallized Material.*

The grain-size developed by annealing after critical deformation is large in pure metals³ and some alloys,⁴ but this large grain-size is invariably associated with a very small critical deformation. In the more complex alloys of the present investigation, the large critical deformation necessary, even where high annealing temperatures were employed, resulted in relatively fine-grain structures under all conditions of processing. The critical rolling reduction was greatest when the alloy was quenched from 500° C. prior to rolling, and least when slowly cooled at this stage. It would thus appear that the critical value is influenced by the proportions of the elements copper and magnesium present in solid solution, for both elements are partially rejected from solution by the slow cooling treatment imposed. The relatively large critical reduction required even in the slowly cooled alloy might also be associated with the presence of manganese, for this element has been shown to increase critical reduction in non-age-hardening alloys.⁴ Since for any one annealed condition maximum grain-size on heat-treatment is found in the sample subjected to the critical reduction, and since grain-size decreases with increasing defor-

mation, it follows that large grain-size is associated with material having a low critical deformation resulting from slow cooling at the annealing stage. This slow cooling, however, results in a further increase in grain-size on final heat-treatment which must presumably be associated with the change in lattice structure, and is consistent with the diminished rate of work-hardening observed by Cook and Richards¹ in material annealed under conditions favouring the rejection of solute atoms.

With rolling reductions well beyond the critical value, i.e. in the range 30-70%, the grain-size for any given reduction was independent of the condition of the alloy prior to rolling, provided it was recrystallized. This again would be expected, for it is known that cold working accelerates precipitation from supersaturated phases, and after sufficiently heavy rolling the composition of the matrix by the time it reaches recrystallization temperature is practically independent of earlier conditions.

Evidence from both the last annealing and final heat-treatment operations indicated that after a heavy rolling reduction, the only factor influencing grain-size, other than the magnitude of the reduction, was the rate of heating. From a consideration of the present state of knowledge of the mechanism of recrystallization, it is probable that this could only result from differences in the temperature range over which recrystallization occurs for the two rates of heating. Since, however, recrystallization was first detected after annealing at 325° C., and was complete at 375° C., while no further increase in grain-size resulted from annealing at higher temperatures, it follows that for both rates of heating recrystallization occurred within a temperature range of 325°-375° C.; the relatively small grain-size variation of about 2:1 would thus seem to be more or less in accordance with expectations.

2. Evidence Regarding the Nature of the Recovered Condition.

Direct evidence of the existence of a distinct recovered state, intermediate between the cold-worked and recrystallized conditions, in an alloy similar to that used in the present investigation, was put forward by Cook and Richards,¹ and the characteristic X-ray diffraction patterns, which consisted of sharply defined continuous rings, were obtained in specimens rolled with reductions ranging from 25 to 90% and annealed at temperatures below 300° C. In the present investigation similar diffraction patterns were obtained in specimens rolled with reductions of less than 10%, that is, below the critical reduction, followed by heat-treatment at 500° C. Material in this condition was compared with recrystallized material prepared by heat-treatment at 500° C. after a heavy rolling reduction, which gave a normal diffraction pattern of

discrete spots. Micro-examination failed to reveal any differences between the recovered and recrystallized conditions, in spite of the differing diffraction patterns. In both conditions the etched grains were stained to distinct shades, which suggested that every grain in each type of material had a definite orientation characteristic of normal recrystallized material. Mechanical properties and age-hardening characteristics were likewise apparently identical in recrystallized and recovered specimens, provided the two had the same apparent grain-size as determined micrographically, but measurable differences in these properties were observed in specimens differing in real or apparent grain-size.

If the character of the diffraction pattern for material in the recovered condition is to be interpreted as indicating the grain-size, this value must be of the order of 0.001 mm. or smaller. This would only be possible if the much larger grains observed under the microscope were regarded as consisting of aggregates of mosaic units, differing so little in orientation in any one grain that the uniform shading observed can be ascribed to light reflections from the etched surface sufficiently parallel to create the appearance of single grains. Such small angular dispersion of mosaic units within individual grains would be sufficient to account for the continuous diffraction rings observed in X-ray patterns.

Since a difference in grain-size, in both recovered and recrystallized specimens, results in a measurable difference in mechanical properties, it is clear that boundaries between mosaic units must differ from those between grains in regard to their effect on mechanical properties and age-hardening characteristics, and that in fact the postulated mosaic aggregates behave mechanically as single grains.

ACKNOWLEDGEMENTS.

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THE INFLUENCE OF OVER-AGEING AND 1173 ANNEALING ON THE HARDNESS AND MICROSTRUCTURE OF AN ALUMINIUM ALLOY TO BRITISH STANDARD SPECIFI- CATION L42.*

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SYNOPSIS.

The effect on its hardness and microstructure of heating B.S.S. L42 aluminium alloy (Hiduminium R.R. 59) for various periods to temperatures between 150° and 400° C. was investigated, with the object of deriving the operating temperature of engine components from a subsequent hardness and microscopic determination. Simple softening curves are obtained at temperatures up to 300° C. but after annealing at temperatures between 300° and 400° C. re-hardening occurs on standing at room temperature and inflections develop in the temperature-hardness curves which render the results ambiguous. The difficulties are resolved by heating the samples to 150°–200° C. for a few hours immediately prior to hardness testing, when smooth curves are again obtained. The progressive changes in microstructure found after heating within the range 215°–400° C. give additional evidence which helps to determine the temperature to which a component has been heated. The variations of lattice parameter with change in annealing conditions were measured, and the results support a tentative explanation of the various phenomena based on present theories of age-hardening.

I.—INTRODUCTION.

A KNOWLEDGE of the operating temperatures of the components of engines of all types is very necessary for the consideration of the suitability of new materials and for the advancement of design. Various methods are available for the determination of such temperatures in special experimental engines, such as the inclusion of thermocouples (the leads being taken through slip-rings or intermittent contacts in the case of moving parts), fusible plugs, temperature-sensitive paints, &c., but the above-mentioned methods involve, to a greater or less degree, some disturbance of the normal conditions of the component, and in many cases are not applicable for one reason or another. Thus it frequently happens that an engine has been tested with none of these special de-

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vices fitted, and an indication of the operating temperature of certain parts is required. In such a case, any permanent change in the physical or mechanical properties of the component which can be directly related to the temperature affords a method of determination, and in this category can be included methods based on the softening of hardened steels, the formation of temper colours, and the over-ageing of precipitation-hardened alloys. The latter effect has been found to be of particular value when applied to aluminium alloys, since over-ageing usually commences at temperatures between 150° and 200° C. and extends over a fairly wide range of temperature which includes the operating temperatures of many engine components.

The aluminium alloy perhaps most commonly used in this country for service at temperatures above 200° C. is Hiduminium R.R. 59 (B.S.S. L42), and this has been very widely employed for aero-engine pistons operating at temperatures exceeding 300° C. In order to obtain the fundamental curves relating hardness to temperature and time of operation, the work now to be described was undertaken.

While these investigations were being carried out, a confidential report ¹ was issued by the Aeronautical Research Council of the Ministry of Aircraft Production describing work done by the Metallurgy Division of the National Physical Laboratory, which covered an investigation of the recovery-hardness values of a number of aluminium-base alloys including R.R. 59. Over the range of time and temperature in which the results can be compared with those given in the present paper, satisfactory agreement is shown.

II.—ANNEALING AT TEMPERATURES UP TO 300° C.

The effect of annealing R.R. 59 at temperatures up to 300° C. is one of straightforward precipitation and softening, uncomplicated by the effects of partial re-solution which become apparent at higher temperatures. It has, therefore, been found convenient to divide the work into two Sections covering the two temperature ranges, both for this reason and because the lower range was covered at an earlier date and with a different batch of material. For the results in this Section we are indebted to Mr. P. H. Frith, who carried out this earlier work.

1. *Material and Heat-Treatment.*

The material used for this part of the work was 1-in.-dia. wrought bar supplied by High Duty Alloys Ltd., and of the following composition : copper 2.02, nickel 1.10, iron 1.03, magnesium 1.43, silicon 0.84, titanium 0.06%, manganese trace, aluminium balance. Test-pieces 3 in. long

were cut from the bar, solution treated at 520° C. for 2 hr. and quenched in boiling water, and aged at 200° C. for 10 hr. This is the treatment normally used for certain aero-engine pistons.

2. Test Procedure and Results..

The bars were annealed at temperatures between 150° and 300° C. at intervals of 25°, in small electric muffle furnaces, and were removed, cooled to room temperature, and tested for hardness at intervals. The

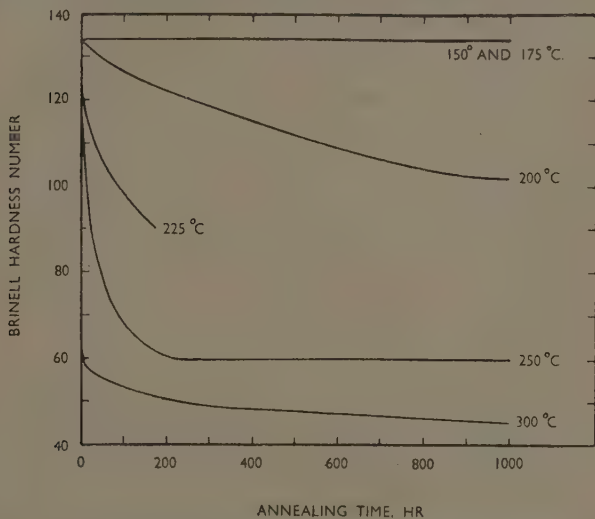


FIG. 1.—Hardness of R.R. 59 After Annealing at Various Temperatures up to 300° C. for Various Times.

hardness tests were made on a Jackman Brinell machine, using a load of 1000 kg., a 10-mm.-dia. ball, and a loading time of 30 sec. The results obtained, plotted in the form of hardness-time curves for the different temperatures are given in Fig. 1, and it is apparent that the softening proceeds progressively at all the temperatures explored.

III.—ANNEALING AT TEMPERATURES BETWEEN 300° AND 400° C.

1. Exploratory Tests.

The curves obtained for temperatures below 300° C. have been used from time to time with success to determine the operating temperature of certain engine components, but it became apparent, when attempts

were made to use the curves in connection with the examination of pistons, that it would be necessary to extend the standard curves to higher temperatures and that the added complexity introduced by partial solution at the annealing temperature would make a more detailed study essential. A preliminary examination of the effects involved was made on an aero-engine piston of which the temperature distribution during running was required. The component had been operated for a total time of 66 hr. and had lain by at normal temperature for

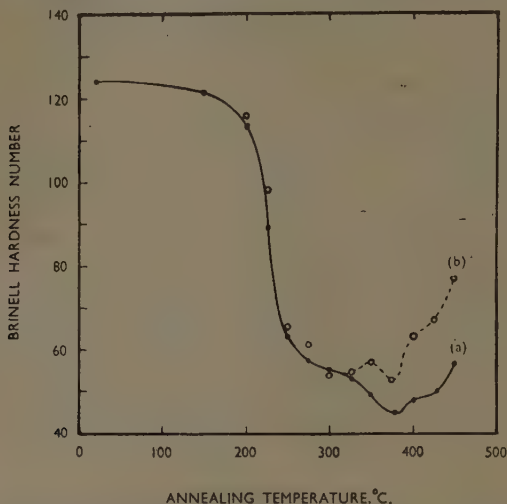


FIG. 2.—Hardness of R.R. 59 Annealed for 66 hr. : (a) immediately after annealing; (b) after ageing at normal temperature for 34 days.

about 12 months before the examination was commenced. This examination was carried out according to the following schedule :

(i) The component was cut along a diameter and a hardness exploration made across the section.

(ii) The component was heat-treated again to recover the original hardness.

(iii) Small portions were annealed for 66 hr. at temperatures at intervals of 25° between 150° and 450° C. and cooled in air.

(iv) The hardness of each portion was measured so that a hardness-temperature curve could be plotted and used to convert the original hardness values to equivalent temperatures.

The experimental conditions involved were the same as described

in Section II, except that the hardness determinations were made on a Vickers machine using a load of 125 kg., a 5-mm.-dia. ball, and a loading time of 30 sec. The smaller ball was necessary in order to obtain a sufficient number of impressions across the section of the component.

The hardness-temperature conversion curve obtained is shown in Fig. 2. Using curve (a) of Fig. 2 attempts were made to convert the hardness values of the original exploration to equivalent temperatures, but although the ambiguity between temperatures above and below the minimum in the curve was borne in mind, it was not possible to derive a rational set of isothermals. The hardness of each standard sample was, therefore, again determined after standing at normal temperature for 34 days, in order to discover the effect of such ageing on the calibration curve, and the broken curve (b) of Fig. 2 was then obtained. The double inflection in the curve now made it clear that any attempt to derive isothermals from a set of hardness readings and such a calibration curve would lead to very unreliable results when the temperatures exceeded about 300° C., but the form of the curve was thought to be of such interest that a detailed investigation of the development of the second inflection on ageing at normal temperature was decided upon.

2. Material and Initial Heat-Treatment.

The whole of the remainder of the investigation was carried out on material supplied by High Duty Alloys Ltd., in the form of 1-in.-dia. wrought bar of the following analysis: copper 2.25, nickel 1.36, iron 1.20, magnesium 1.53, silicon 0.80, titanium 0.06, manganese 0.08%, aluminium balance. The test-pieces were 6 in. long and were solution treated at 520° C. for 2 hr., quenched in boiling water and aged at 200° C. for 10 hr.; the various annealing treatments were then carried out on the test-bars in this form.

3. Hardness Testing.

All measurements of hardness were made with the Vickers machine using a load of 125 kg., a 5-mm.-dia. ball and a loading time of 30 sec. Small samples about $\frac{1}{2}$ in. long were cut from the test-bar, polished on the sectioned face and the impressions made on this surface, care being taken that no impressions were made on a surface which had been adjacent to the surface layers during heat-treatment, as it is known that slight preferential oxidation of magnesium can occur with a consequent reduction in hardness of the immediate surface layers. The values quoted are always the mean of two or three separate readings.

4. *Effect of Time of Annealing and Time of Subsequent Ageing at Normal Temperature.*

The annealing temperatures selected for test were 300° , 325° , 350° , 375° , and 400° C., and one bar was annealed at each of these temperatures for each of the following times : 4, 20, 50, and 100 hr. At the conclusion of the annealing period the test-bar was allowed to cool normally on a tray of sand. Small samples were parted off and prepared for hardness testing, and tests were carried out, initially 1 hr. after the

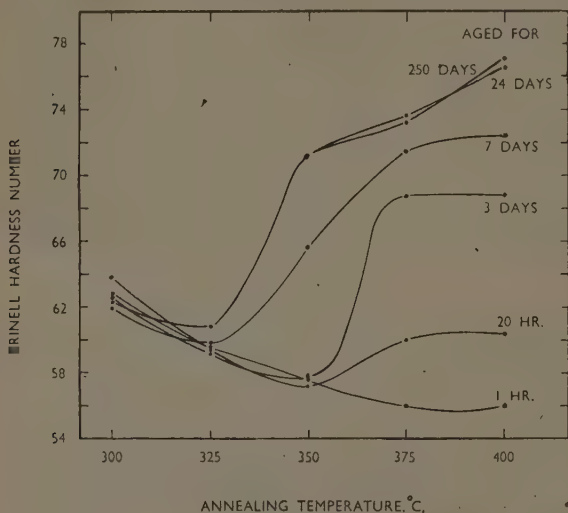


FIG. 3.—Hardness of R.R. 59 After Annealing for 4 hr. and Ageing at Room Temperature.

completion of annealing, and subsequently after total ageing times of 6 hr., 20 hr., 3 days, 7 days, 14 days, 24 days, and finally at longer intervals up to a total of about 1 year. The results obtained are best given graphically and Figs. 3, 4, 5, and 6 show the families of curves obtained for annealing periods of 4, 20, 50, and 100 hr., respectively. All the curves obtained have not been included, the times of normal-temperature ageing shown being those which give the clearest indication of the trend of the changes.

For annealing temperatures of 300° and 325° C. it is apparent that the time of ageing at normal temperature is of little importance, but there is still a progressive falling in hardness with times of annealing

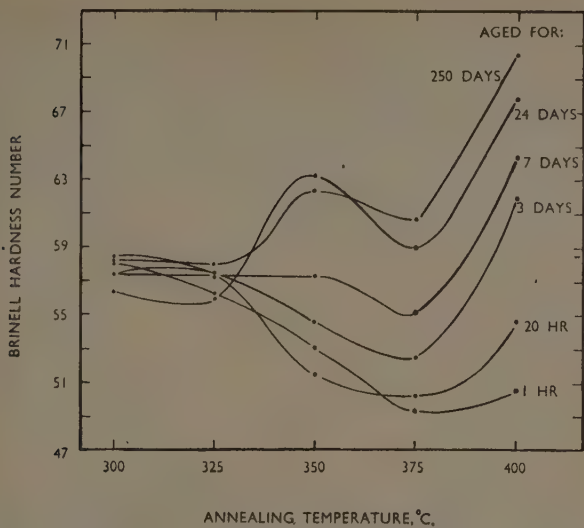


FIG. 4.—Hardness of R.R. 59 After Annealing for 20 hr. and Ageing at Room Temperature.

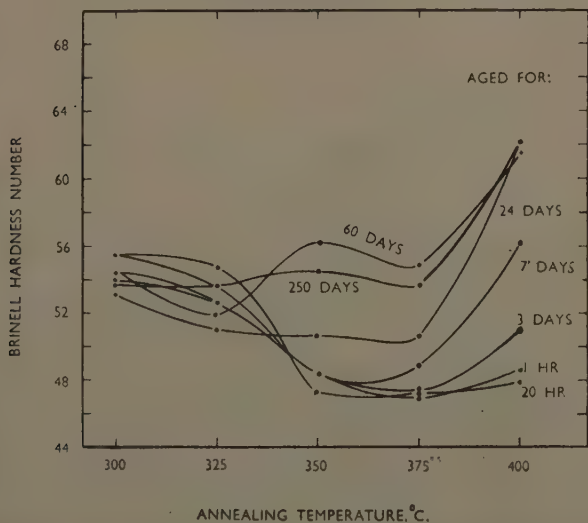


FIG. 5.—Hardness of R.R. 59 After Annealing for 50 hr. and Ageing at Room Temperature.

between 50 and 100 hr.; that is, the alloy is not completely annealed even after 50 hr. at 325°C . After annealing at temperatures of 350°C . and above, hardening on ageing at room temperature occurs, commencing after about 3 days' ageing and reaching its maximum after about 24 days; but the increase in hardness after annealing at 350°C . is in general as great as that after annealing at 375°C . and, on account of the initially higher hardness due to less complete annealing, leads to the formation of a hump in the curve in this region. For a period of annealing of

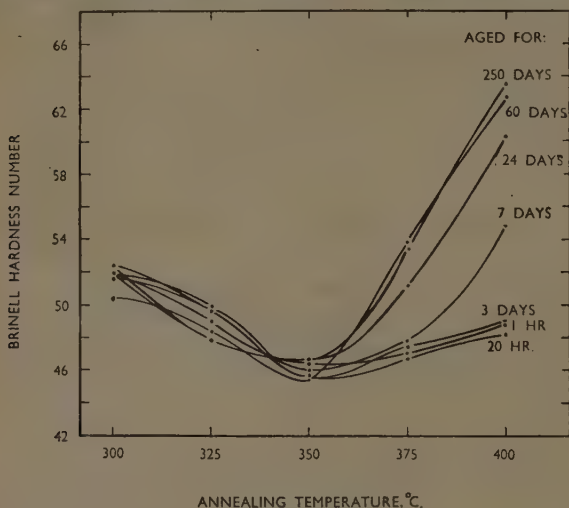


FIG. 6.—Hardness of R.R. 59 After Annealing for 100 hr. and Ageing at Room Temperature.

100 hr., however, no hardening occurs for an annealing temperature of 350°C . and no hump appears.

In order to obtain a more precise indication of the shape of the hardness-temperature curve and of the temperature at which the hump forms, a bar of the 1-in.-dia. material, about 18 in. long, was heat-treated in the standard manner and threaded at one end to screw into a copper block on which was wound a heating element. Thermocouples were fitted into small holes drilled into the bar at intervals of 2 in. along its length, and the whole assembly was placed in a container packed with Kieselguhr. The free end of the bar was allowed to project slightly from the insulating material and conditions were adjusted so that a fairly uniform temperature gradient from 415° to 280°C . was obtained

along the length of the bar. The temperature of the heater block was controlled with a Cambridge regulator and the bar was annealed in this manner for a period of 20 hr. from attaining stability of temperature, which had taken 2 hr. from commencement of heating. During the period of annealing all the temperatures of the bar remained constant

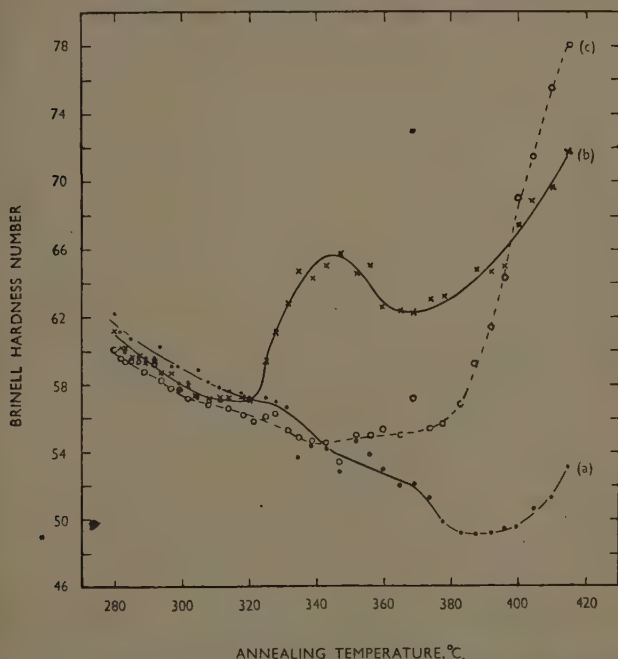


FIG. 7.—Hardness-Temperature Curves for R.R. 59 Obtained from Bar with Temperature Gradient, Annealed for 20 hr.

- (a) After ageing at room temperature for 7 hr.
- (b) After ageing at room temperature for 26 days.
- (c) After accelerated ageing for 10 hr. at 200° C.

to within $\pm 1^\circ \text{C.}$ and the average gradient was about 10°C./in. , so that, by making hardness measurements at intervals along the bar, an accurate relationship between temperature of annealing and hardness could be derived with individual readings only 5°C. apart in annealing temperature. In this manner the curves shown in Fig. 7 were obtained; (a) is the curve obtained shortly after annealing, (b) is that after ageing at normal temperature for 26 days and shows the re-hardening effect

with the inflection at about 350° C., while (c) is the curve after heating to 200° C. for 10 hr., which will be dealt with later.

5. *Effect of Interrupted Annealing with Intermediate Ageing at Normal Temperature.*

It is frequently the case that the testing or running of an engine is not continuous, so that the total time of a component at its operating

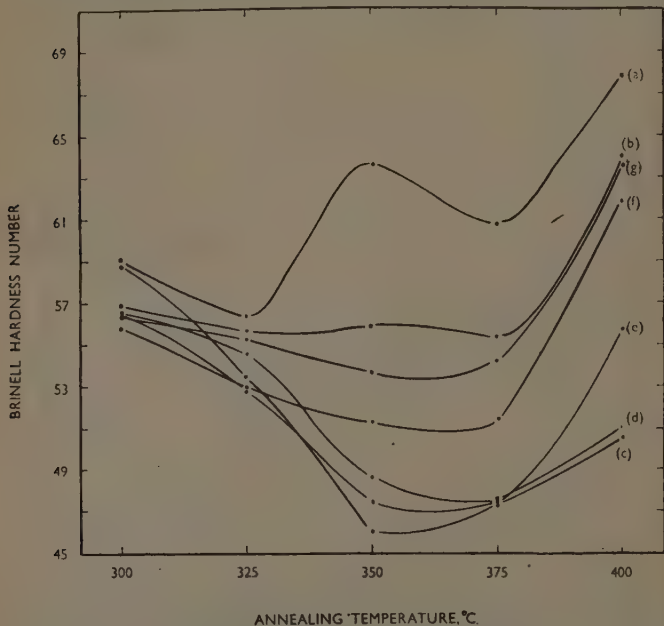


FIG. 8.—Hardness-Temperature Curves for R.R. 59 After Interrupted Annealing Treatments.

- (a) After 16 hr. anneal and 28 days' ageing.
- (b) After 16 hr. anneal and 28 days' ageing, twice (32 hr. total anneal).
- (c) After 16 hr. + 16 hr. + 18 hr. anneal, and 1 hr. ageing.
- (d) After 16 hr. + 16 hr. + 18 hr. anneal, and 3 days' ageing.
- (e) After 16 hr. + 16 hr. + 18 hr. anneal, and 7 days' ageing.
- (f) After 16 hr. + 16 hr. + 18 hr. anneal, and 24 days' ageing.
- (g) After 16 hr. + 16 hr. + 18 hr. anneal, and 220 days' ageing.

temperature is made up of several shorter periods separated by periods of standing at normal temperature. It is clearly desirable that this should not have a disturbing influence on the hardness-temperature

conversion curves, and to investigate this point, test samples were annealed for a total period of 50 hr. at the same temperatures between 300° and 400° C. as before, the total time being made up of three periods of 16, 16, and 18 hr., with intermediate rests at normal temperature of 28 days. Hardness measurements in this case were made after the first 16 hr. anneal and 28 days' ageing, again after the second 16 hr. anneal and 28 days' ageing, and then after the completion of the total annealing period at the necessary intervals to determine the course of any re-hardening. The results obtained are illustrated in Fig. 8. Curve (a) shows the expected hump in the curve obtained after the initial 16 hr. annealing followed by 28 days' ageing, but curve (b), after the second such anneal and ageing, has a much less marked inflection; while the remaining curves, after the completion of the total of 50 hr. annealing, show no inflection even after 220 days' ageing.

Since the curves (c) to (f) of Fig. 8 are not identical with those of Fig. 5 for corresponding times of ageing at normal temperature, it became apparent that these curves could not be used for the determination of annealing temperature from the subsequent hardness measurements unless the running programme of the engine was very closely recorded, and calibration curves would probably require to be determined afresh for every variation in the programme.

6. Effect of Accelerated Ageing after Annealing.

The relatively slow progress of ageing at normal temperature, as evidenced by the curves shown in Figs. 3-6, would make it necessary either to wait until some stability in hardness was reached after about 28 days, or to use a family of calibration curves, and even then the varying conditions of running would again require different curves, as indicated in the previous Section. It appeared possible that some or all of these difficulties could be overcome by an accelerated ageing treatment, which would produce the stable conditions characteristic of several thousands of hours' ageing at normal temperature, after only a few hours at some slightly elevated temperature. To investigate the effect of such accelerated ageing one test bar of the standard size was annealed for 20 hr. at each of the usual temperatures and then allowed to age at normal temperature for 28 days to develop the inflection in the temperature-hardness curve (curve (a), Fig. 9). Hardness test samples were then cut and prepared and one from each test bar was aged by each of the following methods: (b) 48 hr. at 150° C.; (c) 10 hr. at 200° C.; (d) 20 hr. at 200° C. These conditions were selected as being treatments which give the maximum hardness after normal solution treat-

ment and can, therefore be considered as bringing all the material in solution to the condition giving the highest hardness. The rate of change of hardness with time of ageing at 200° C. is very slow after about 10 hr. so that treatment (d) would, after normal solution treatment, give the same hardness as treatment (c). The curves obtained after these treatments are given in Fig. 9, and it is seen that all three accelerated ageing treatments lead to essentially the same curve, with the complete

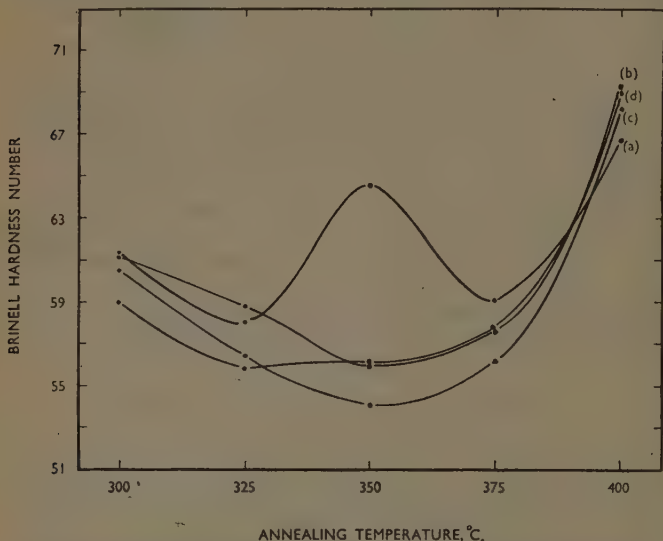


FIG. 9.—Hardness-Temperature Curves for R.R. 59 After Accelerated Ageing Following 20 hr. Annealing.

- (a) 28 days at room temperature.
- (b) 28 days at room temperature + 48 hr. at 150° C.
- (c) 28 days at room temperature + 10 hr. at 200° C.
- (d) 28 days at room temperature + 20 hr. at 200° C.

elimination of the hump at 350° C. produced after ageing at normal temperature. The hardness determinations leading to curves (b), (c), and (d) of Fig. 9 were made at intervals of 4 hr., 43 hr., and 25 hr., respectively, after the completion of the accelerated ageing treatment and, although it is of little practical importance—since hardness testing can always be carried out within this period after such ageing, although not always so shortly after engine running—the effect of subsequent ageing at room temperature was also investigated. After 28 days

the hardness-temperature curves had partially reverted to the shape of curve (a) and the hump in the region of 350° C. was clearly marked.

Since accelerated ageing was successful in removing the inflection from the hardness-temperature curve, it became necessary to determine whether it was effective in smoothing out the differences between con-

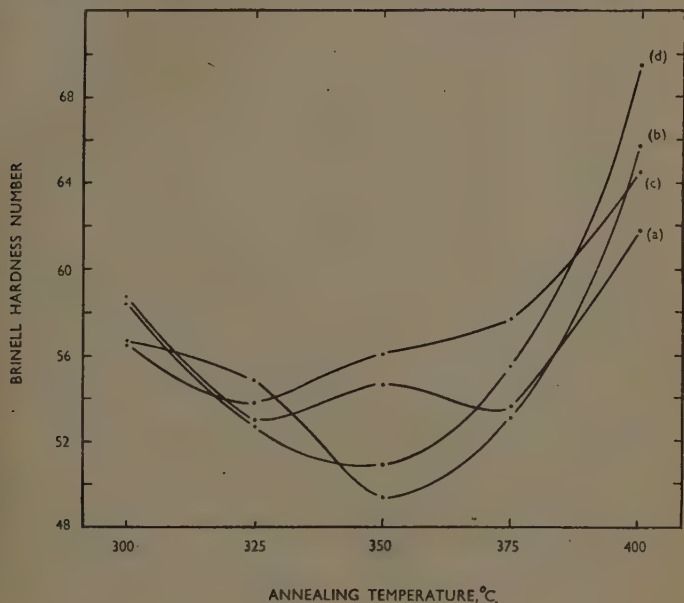


FIG. 10.—Hardness-Temperature Curves for R.R. 59 Annealed for 50 hr. and Aged.

- (a) Continuous anneal; aged 28 days at normal temperature.
- (b) Continuous anneal; aged 28 days at normal temperature + 10 hr. at 200° C.
- (c) Interrupted anneal; aged 28 days at normal temperature.
- (d) Interrupted anneal; aged 28 days at normal temperature + 10 hr. at 200° C.

tinuous and interrupted annealing. For this purpose new test samples were heat-treated and annealed for 50 hr. at the usual five temperatures, one sample being annealed for 50 hr. continuously, while a second was annealed in three periods of 16, 16, and 18 hr., with 28 days' ageing at normal temperature in between each period of annealing. After the completion of the total period of annealing the samples were aged at normal temperature for 28 days and the hardness-temperature curves

(a) and (c) of Fig. 10 were obtained. These two curves confirm, in a general way, those shown in Figs. 5 and 8; except that the hump has developed more rapidly, after the continuous 50-hr. anneal, than it did with the earlier samples treated similarly; and that the results obtained after the interrupted 50-hr. anneal indicate a considerably greater degree

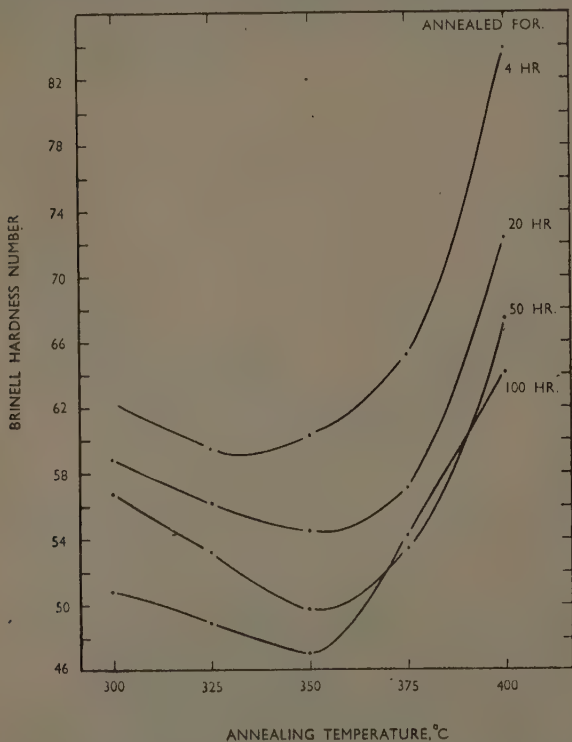


FIG. 11.—Hardness-Temperature Curves for R.R. 59 After Ageing at 200° C. for 10 hr.

of re-hardening after annealing at 350° and 375° C. than was shown with the earlier samples treated similarly.

All the samples were then aged at 200° C. for 10 hr. and again tested for hardness; and, as is shown in Fig. 10, the two curves (b) and (d) then obtained, corresponding to the continuous and interrupted annealing treatments, were essentially the same.

It thus appeared that by ageing at 200° C. for 10 hr., the disturbing effects of interruptions in the period of annealing and of slow re-hardening on standing at normal temperature could be eliminated; and in order to confirm that for a given total period of annealing and independent of the period of ageing at normal temperature, a constant curve relating hardness and annealing temperature is obtained, all the samples used in the previous tests were aged in this manner. For a given time of annealing a constant curve was obtained, independent of the time of ageing at normal temperature prior to the accelerated ageing. The average curves obtained from all the samples annealed for 20 and 50 hr. are shown in Fig. 11. The single sets of samples annealed for 4 hr. and 100 hr., were aged similarly and the resultant curves are also included in Fig. 11. The 18-in. bar used for the more accurate determination of the position of the inflection was aged at 200° C. for 10 hr. and the resultant curve is shown in Fig. 7 (curve (c)).

In order to investigate the effect of accelerated ageing at 200° C. applied immediately after the annealing treatment without intermediate room-temperature ageing, a series of samples was annealed for 20 hr. at the same five temperatures as before, air cooled, and then immediately aged at 200° C. for 10 hr. The resulting hardness-temperature curve did not correspond with that obtained on ageing at 200° C. after the intermediate room-temperature ageing. No re-hardening resulted for any annealing temperature below 400° C. and the re-hardening with the 400° C. annealing temperature was very slight compared with that produced by room-temperature ageing. It was thus obvious that the curves of Fig. 11 could only be applied when a sufficient period of room-temperature ageing had elapsed between the annealing and the accelerated ageing treatments.

7. Lattice Parameter Measurements.

In order to assist in the explanation of the observed hardness phenomena, measurements of the lattice parameter of the alloy were made in parallel with the hardness determinations described in Section III. 4. For this purpose filings were prepared from a heat-treated bar and were then enclosed in an evacuated silica tube and again solution treated and precipitation-hardened in the standard manner. The filings were then divided into a number of portions, each of which was again sealed in an evacuated Pyrex tube and annealed with the hardness test samples at temperatures between 300° and 400° C. for varying times. Parameter measurements were then made at intervals during the course of ageing at normal temperature.

A back-reflection focusing camera of the Seeman-Bohlin type, 9 cm. in dia., was used, in which the sample was held on the same circumference as the film and, in order to obtain continuous lines, was oscillated about the centre of the camera through an angle of about 10° during the course of the exposure. $\text{CuK}\alpha$ radiation was used and gave reflections from the (333) planes at an angle of about 82° and from the (422) planes at an angle of about 68° . The lattice parameter was calculated separately for these two reflections and by extrapolating against the function $\frac{1 + \cos 2\theta}{\cos 2\theta}$ to $\theta = 90^\circ$, was corrected for errors in the location of the specimen with respect to the circumference of the camera (see Appendix, p. 663). The parameter values were reduced to 20°C. and are considered accurate to 0.0001 kX.

The results obtained showed that in no case did any significant change in parameter occur with ageing at normal temperature, even though marked variations in hardness were found. This is in conformity with expectation, since no parameter change is observed with increase of hardness on normal precipitation-hardening. Clearly marked changes occurred, however, with variation in time and temperature of annealing and these are summarized in Table I.

TABLE I.—*Lattice Parameters of R.R. 59 in kX.*

Value when solution treated 2 hr. at 520°C. and quenched in boiling

water

4.0387₅ kX.

Value when solution treated as above and aged at 200°C. for 10 hr.

4.0389₅ kX.

Annealing Temperature, $^\circ \text{C.}$	Annealing Time			
	4 hr.	20 hr.	50 hr.	100 hr.
300°	4.0403	4.0401 ₅	4.0403	4.0401 ₅
325°	4.0401	4.0399 ₅	4.0399	4.0400
350°	4.0395	4.0397	4.0398	4.0397 ₅
375°	4.0391 ₅	4.0393	4.0393 ₅	4.0395 ₅
400°	4.0391	4.0393 ₅	4.0394 ₅	4.0394

IV.—EFFECT OF ANNEALING TREATMENTS ON THE MICROSTRUCTURE.

In conjunction with the exploratory hardness tests described in Section III. 1., carried out on small specimens from the piston after a total operating time of 66 hr., parallel specimens were prepared for microscopic examination. The specimens were prepared from the component after re-heat-treatment and were metallographically polished after annealing at selected temperatures between 150° and 450°C. and air cooling. Between 215° and 450°C. temperature intervals of 15°

were chosen, but it was considered to be unnecessary to examine specimens annealed at temperatures between 150° and 215° C. All specimens were annealed for 66 hr. at the selected temperatures.

After polishing, the specimens were etched for 1 min. in an aqueous solution containing 25% nitric acid, used at 70° C.

The structures observed are illustrated in Figs. 12-17 (Plates LXXXIV and LXXXV) at a magnification of 1000 dia.

After annealing at 150° C. (Fig. 12), the specimen exhibited well-marked grain boundaries and slight indications of intercrystalline precipitation. A very different structure resulted from annealing between 215° and 275° C. and there was a marked increase in the quantity of visible precipitate. The original grain boundaries were slightly denser, a number of the grains showed a moderately coarse, uniform deposition of hardening constituents, and in the remaining grains a very dense precipitation accompanying a "mosaic" grain structure was apparent. These features are illustrated in Fig. 13 and by comparison with Fig. 12 the very definite metallographic changes are readily apparent.

The changes between 215° and 275° C. were gradual and relatively slight, so that a determination of the annealing temperature in this range from the microstructure would be extremely difficult and the hardness test results provide the more reliable guide.

Annealing at 305° C. provided the structure illustrated in Fig. 14 in which the "mosaic" pattern was still evident, but the precipitate had coagulated, providing a less dense distribution. The marked difference in structure of the specimen annealed at this temperature as compared with the specimen annealed at 275° C. provides valuable evidence to supplement the results obtained by hardness tests.

After annealing at 335° C. the precipitate exhibited strong coalescence and presented a lamellar appearance which had not developed at the lower temperatures. The grain boundaries were still evident after annealing at this temperature (see Fig. 15), but the "mosaic" pattern had been largely dispersed.

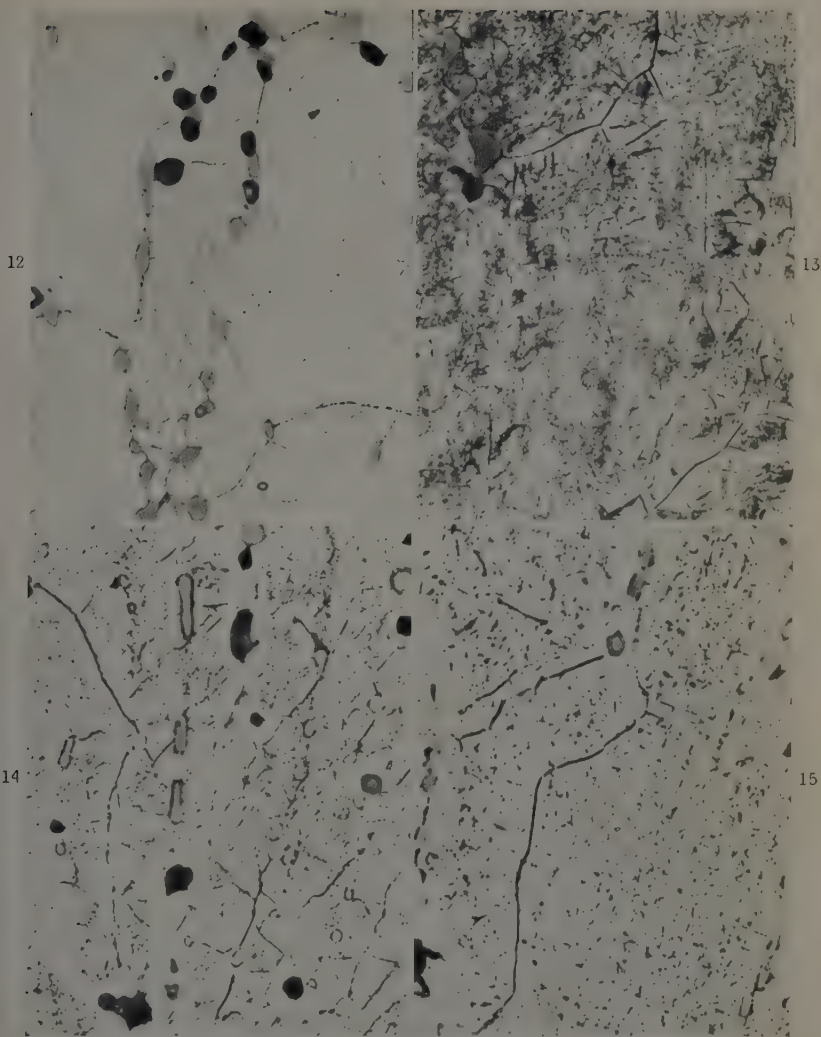
The specimen annealed at 365° C. is shown in Fig. 16, and it will be observed that the precipitate dispersion had changed considerably by comparison with that of the specimen annealed at 335° C. (Fig. 15). The precipitate was comparatively fine, the lamellar appearance had largely been replaced by a spherical condition, and areas of the specimen showed no evidence of the precipitated phase. These features provide evidence of re-solution of the hardening phases and suggest that at a temperature between 335° and 365° C. the aluminium solid solution ceases to be saturated and can again absorb the precipitate. A further

interesting feature of the structure of this specimen is to be found in the absence of grain boundaries. The etching reagent employed was chosen to reveal the precipitated phases, since it darkens copper-bearing compounds preferentially and by this means outlines the grain boundaries when such phases are present. Careful examination of the specimen showed that no grain boundaries were visible, thus indicating that the condition of the solid solution encourages rapid solution of the hardening compounds on heating above the saturation temperature.

It will be recalled that the inflection in the recovery-hardness curve corresponds with an annealing temperature of approximately 350° C. In this region of the curve, unless an accelerated ageing treatment is given, the hardness values provide no reliable guide when used to estimate annealing temperatures, since by virtue of the inflection in the curve a given hardness value can correspond with two or three annealing temperatures. However, annealing temperatures in the region of 350° C. produce the maximum influence on the microstructure and the changes observed may be employed to estimate the annealing temperature. In employing this evidence it must be borne in mind that the rate of cooling from the annealing temperature will influence the observed structure, and due allowance must be made for this factor in attempting to assess the structures observed in components which have operated at high temperatures. Nevertheless, the structures can be taken as a guide and the variations from these standard structures consequent upon the slower cooling rate of larger masses will provide little difficulty as experience is gained.

Annealing temperatures above 365° C. promoted increased re-solution of the hardening phases, as illustrated by Fig. 17 corresponding with 440° C. Above 395° C. estimation of the annealing temperature from the microstructure would present some difficulty, but the recovery-hardness values would form a reliable guide and the microstructure need only be used to provide confirmatory evidence where necessary. The influence on the microstructure of variation in the time of annealing was investigated and Figs. 18-19 (Plate LXXXV) illustrate the structures obtained after annealing times of 19 hr. and 56 hr., respectively, at 245° C. Comparison of these with the structure of Fig. 13 (Plate LXXXIV) indicates that variation within this range has no significant effect on the microstructure.

As has been described, the inflection in the recovery-hardness-temperature curve has caused difficulty in interpretation and therefore, the stabilizing treatment at 200° C. was investigated. By this means a smooth recovery-hardness-temperature curve has been obtained, but it was thought that this treatment would produce an adverse effect on



FIGS. 12-15.—Effect of Annealing Treatments on Microstructure. $\times 1000$.

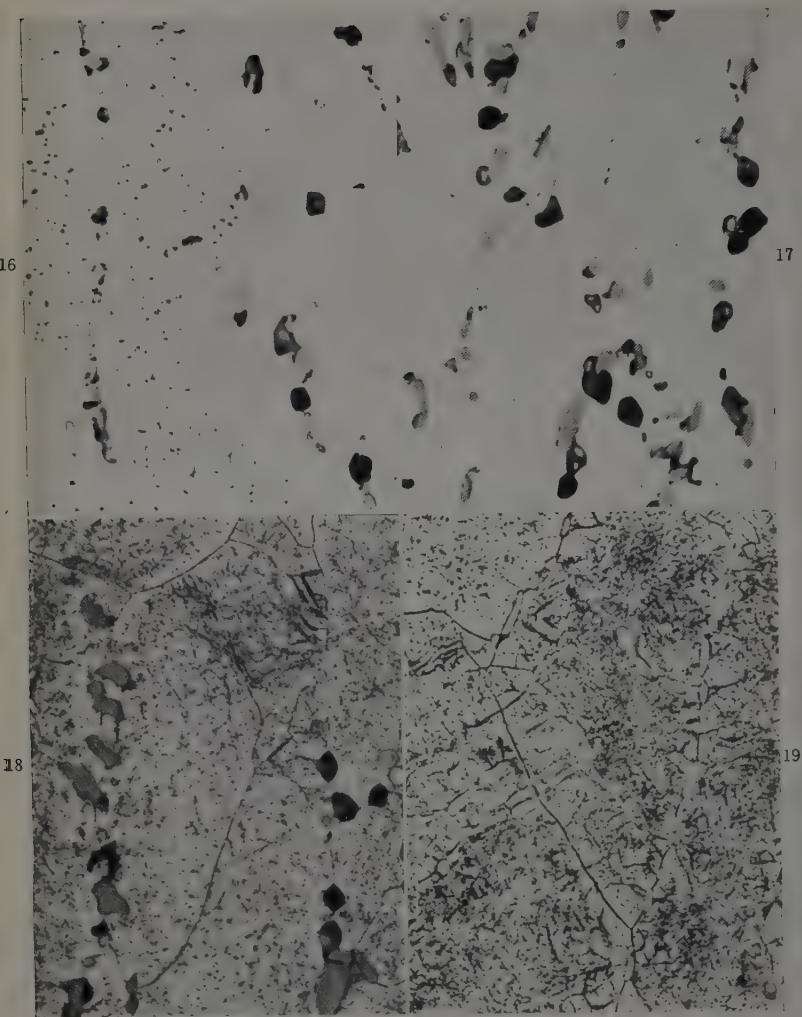
FIG. 12.—Annealed for 66 hr. at 150°C .

FIG. 14.—Annealed for 66 hr. at 305°C .

FIG. 13.—Annealed for 66 hr. at 245°C .

FIG. 15.—Annealed for 66 hr. at 335°C .

[To face p. 658.]



FIGS. 16-19.—Effect of Annealing Treatments on Microstructure. $\times 1000$.

FIG. 16.—Annealed for 66 hr. at 365°C .
 FIG. 18.—Annealed for 19 hr. at 245°C .

FIG. 17.—Annealed for 66 hr. at 440°C .
 FIG. 19.—Annealed for 56 hr. at 245°C .

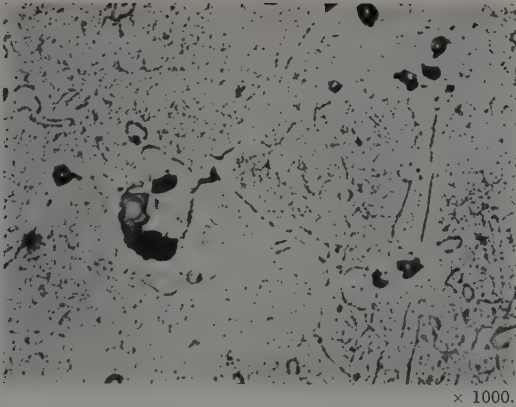


FIG. 20.—Effect on Microstructure of Stabilizing Treatment. Annealed for 20 hr. at 325° C.; aged for 10 hr. at 200° C.

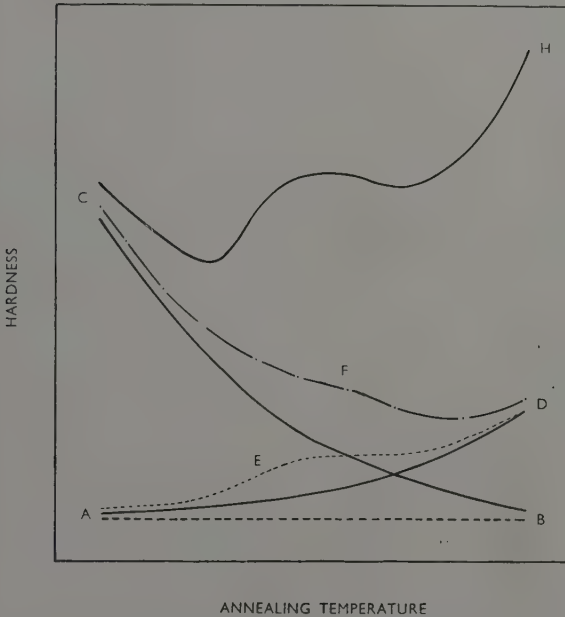


FIG. 21.—Hypothetical Curves Illustrating the Effects of Annealing and Room-Temperature Ageing on Hardness.

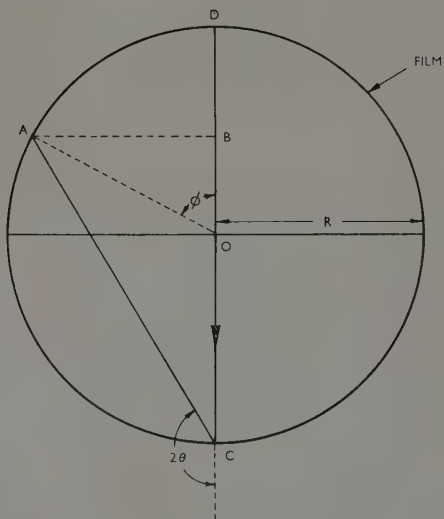


FIG. 22.—Arrangement of Film and Sample for Parameter Measurements.

the data to be obtained from the microstructure. Accordingly a further series of specimens was prepared to investigate the annealing temperatures 300°, 325°, 350°, 375°, and 400° C. After annealing for 20 hr., the specimens were cooled in air and then reheated to 200° C. They were held at this temperature for 10 hr. and again air-cooled to room temperature. The specimens were then prepared for microscopic examination by polishing and etching in the solution employed for the earlier series. It was found that stabilizing at 200° C. had obliterated the structure corresponding with the annealing temperature by promoting a general precipitation which was similar in all the specimens of this group, so that after such a treatment the microstructures cannot be employed to estimate the annealing temperatures. Fig. 20 (Plate LXXXVI) illustrates the effect of the stabilizing treatment on the sample annealed at 325° C.

V.—DISCUSSION OF RESULTS.

The practical application of the results described is straightforward. After annealing at temperatures up to 300° C. no re-hardening occurs on ageing at normal temperature and the annealing temperature can readily be obtained from a measurement of the hardness by the curves of Fig. 1. Metallographic examination, based on the structures shown in Figs. 12–14 (Plate LXXXIV), is less sensitive, but might add useful confirmatory evidence. If annealing temperatures above 300° C. have to be covered, specimens for microscopic examination are first prepared from the component and the annealing temperatures determined on the basis of the structures shown in Figs. 14–17 (Plates LXXXIV and LXXXV). After remaining at room temperature for about 28 days, the remainder of the component is then aged at 200° C. for 10 hr. and hardness tests are made at positions adjacent to those of the micro-specimens; these readings are converted to annealing temperatures by the curves of Fig. 11. The curves are applicable whether the annealing is carried out in one continuous period or in a number of shorter periods with intermediate ageing at normal temperature. The combined results enable a reasonably accurate picture of temperature distribution in a component to be obtained, and the method has been used with success in the case of aero-engine pistons, leading to the construction of a model of isothermal surfaces.

From the theoretical aspect it is of some interest to consider the mechanism of the re-hardening observed on ageing at normal temperature. In the first place, it appeared probable that the inflection at about 350° C. in the curves after ageing at normal temperature was

caused by incipient precipitation of another phase, additional to the one leading to the main re-hardening at somewhat higher temperatures of annealing. Since the hump disappears on heating to 150° or 200° C. and re-forms again on further standing at normal temperature, it would be necessary for this second precipitating phase to be taken into solution at these temperatures and only precipitated at normal temperature. This theory was untenable, however, since it could not explain the absence of the hump after annealing for 100 hr., or the fact that the re-hardening did not occur after annealing at 300° C., at which temperature, as explained above, the proposed phase would need to be held in solution.

The observations indicate that the inflection in the curve occurs after annealing for periods of 4, 20, and 50 hr., but not after 100 hr., and since the hardness after annealing for these periods at 350° C. falls progressively with increasing annealing time, it appears probable that the inflection is connected with incomplete annealing. According to present theories of age-hardening,² the maximum hardness is obtained by the aggregation of atoms of the solutes to form nuclei in the parent lattice of a critical size to give the maximum amount of lattice strain, but still coherent with the lattice so that no change in mean parameter is detectable. At higher temperatures or after longer periods of ageing these nuclei grow in size, and eventually, and probably in conjunction with a change from an unstable intermediate structure to a stable structure, dissociate from the parent lattice, causing a change in lattice parameter and resulting in considerable softening. If the nuclei form at one temperature, a subsequent rise in temperature will cause the nuclei first to re-dissolve, with consequent softening, and then to re-form and again increase the hardness.³ The conception is that at the lower temperatures small nuclei are stable, but with rising temperature, on account of the increased thermal agitation of the atoms, they become unstable and disperse, and a larger nucleus is necessary for stability. These large nuclei originate from fortuitous association of atoms, and thus the chances of such association, and hence the numbers of the nuclei, become less. With these theories in mind it appears possible to go some distance in explanation of the observed hardening phenomena.

In the fully heat-treated state, in which the annealing of the alloy was commenced, precipitation has proceeded to such a degree that the hardness is a maximum, but no change of lattice parameter has occurred from that of the solution-treated condition. This suggests that the precipitation up to this stage is of the discontinuous type,⁴ and the nuclei which have formed have produced severe strains in the lattice without changing the composition of the bulk of the solid solution. On

annealing at the temperatures investigated in the present work it is suggested that softening is effected by two mechanisms which proceed to some extent independently of each other: the first is a relief of the existing lattice strain, and the second is the precipitation of the remaining solute atoms from the supersaturated matrix. The relief of strain proceeds at a rate which is very dependent on temperature, so that on annealing at the lowest temperature of 300° C. the rate would be much slower than on annealing at temperatures around 400° C., and after a constant but limited period of annealing the residual strain would be less with increasing annealing temperature.

The rate of precipitation from the original solid solution, however, is thought to be related to the annealing temperature in a more complex manner. Whereas the diffusion rate increases with increasing temperature, the degree of supersaturation, which determines the potential gradient of the diffusion process, falls with rise of temperature; and also, since the size and separation of the particles on to which precipitation is taking place is greater at higher temperatures, the average distance which a solute atom has to travel is increased. The result is that it appears quite possible for an inflection to occur in the curve relating rate of precipitation to annealing temperature, and it is suggested that, in the present case, the rate is high at 300° C. owing to the small distance which a precipitating atom has to travel, lower at 350° C. owing to the increasing distance of travel, but high again at 375° C. and above on account of the increasing rate of diffusion. These suggestions are borne out by the parameter measurements to the extent of the accuracy attained, for while on annealing at 300° or 325° C. the parameter has reached the equilibrium value after only 4 hr., on annealing at 350° C. or higher there is a progressive increase in parameter with time of annealing; there was no evidence from this source, however, that the rate of precipitation was faster again at 400° C.

The results which follow from these suggestions as to the mechanism of annealing can best be illustrated diagrammatically and Fig. 21 (Plate LXXXVI) is an attempt to do this. The dotted line *AB* represents the hardness level of the fully annealed solid solution in equilibrium at normal temperature and the curve *CB* represents the hardness due to the residual lattice strain after annealing for a fixed period at varying temperatures; as previously described this strain will fall with increasing temperature. The curve *AD* represents the hardness of the fully annealed solid solution saturated at the annealing temperature, i.e. with no hardness contribution due to the residual lattice strain of curve *CB*. Since the equilibrium composition is not attained with restricted periods of annealing, the actual hardness of the solid solution will be represented

by the dotted curve *AED*, in which the departure from equilibrium is made greatest in the middle region of temperature for the reason described earlier. Thus the final hardness of the annealed alloys immediately after cooling to normal temperature will be represented by the sum of the curves *CB* and *AED*, namely *CFD*. Now, on ageing at normal temperature, hardness increments will be observed in proportion to the amount of solute material above the normal-temperature equilibrium concentration and, therefore, proportional to the height of the curve *AED* above the line *AB*. If such increments are added to the curve *CFD* a humped curve such as *CH* is obtained, the original hump assumed in the curve *AED* being exaggerated in proportion to the amount by which precipitation-hardening is assumed to exceed solid solution hardening. If annealing were prolonged so that the solid solution reached the equilibrium concentration represented by the continuous curve *AD*, no hump would be found in the final hardness curve, and this is apparently the condition achieved after 100 hr. annealing.

The mechanism proposed can thus explain the shape of curve obtained immediately after annealing for various periods and also after ageing at normal temperature.

The softening observed on ageing at 200° C., which results in the removal of the hump from the curve, can be explained as a restoration phenomenon, i.e. re-solution of precipitated nuclei; but since restoration as normally understood is completed in a few minutes and further precipitation then takes place with consequent re-hardening, it is necessary, in this case, to postulate that a certain degree of supersaturation needs to exist for precipitation to occur. Thus, after annealing at 350° C. for a limited period, the amount of material retained in solution is sufficient to precipitate on ageing at normal temperature, but subsequent heating to 200° C. dissolves the nuclei thus formed and there is not sufficient supersaturation at 200° C. for the solute to re-precipitate. After annealing at 400° C., however, it is possible that the amount of material held in solution is sufficient to precipitate either at normal temperature or at 200° C. and that no restoration phenomenon was observed merely because very short times of ageing at 200° C. were not investigated.

The observed hardening on ageing at 200° C. immediately after the completion of the annealing treatment appears to agree with this supposition as to the influence of degree of supersaturation, for after annealing at temperatures up to 375° C. no hardness increment is observed on ageing, and the increment after annealing at 400° C. is small compared with that produced by ageing at normal temperature, owing to the decreased amount of supersaturation.

It seems that ageing at normal temperature is necessary to produce the highest hardness increment after annealing at 400° C., and while further ageing at 200° C. does not cause the hardness attained to drop and may even increase it, such ageing without the initial normal-temperature ageing produces a much less marked effect. This last observation suggests that the restoration phenomenon only involves complete resolution when the amount of precipitated material is not too great, and that precipitation at 200° C. without prior normal-temperature ageing only takes place above a certain level of supersaturation.

Alternatively, it could be proposed that normal-temperature precipitation is discontinuous, thus producing strain-hardening, but that the precipitation at 200° C. after the lower-temperature annealing treatments is continuous, on account of the lower degree of supersaturation, and therefore this produces no hardening. On the other hand, after annealing at 400° C. the supersaturation is sufficient to give discontinuous precipitation, and therefore an increase in hardness, when ageing is carried out at 200° C. No parameter measurements were carried out after these ageing treatments, so that it is not possible to decide which suggestion more nearly corresponds to the truth.

ACKNOWLEDGEMENTS.

In conclusion the authors wish to express their appreciation of the help given by various staff members in the experimental work, and to thank the two firms concerned, High Duty Alloys Ltd. and the Bristol Aeroplane Co. Ltd., for permission to publish.

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APPENDIX.

EXTRAPOLATION OF PARAMETER VALUES TO ALLOW FOR ERRORS IN SPECIMEN LOCATION.

In Fig. 22 (Plate LXXXVII) the incident beam DC falls on the sample at C and is diffracted along CA to be recorded on the film at A . It is required to find, for a constant position of the trace A , how the diffraction angle θ varies with variation in the position of the

sample with respect to the centre of camera, that is of the distance $OC = D$.

$$\tan (180 - 2\theta) = \frac{AB}{BC} = \frac{R \sin \phi}{OC + BO} = \frac{R \sin \phi}{D + R \cos \theta}$$

$$\text{Differentiating} \quad \frac{d\theta}{dD} = \frac{\sin^2 2\theta}{2R \sin \phi} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{From } \lambda = 2d \sin \theta \quad \frac{dd}{d\theta} = -d \cot \theta \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{From (1) and (2)} \quad \frac{dd}{dD} = \frac{-d \cot \theta \cdot \sin^2 2\theta}{2R \sin \phi}$$

Since the point C is very nearly on the circumference of the camera we can put $\phi = 2\pi - 4\theta$ and hence

$$\frac{dd}{d} = \frac{\cot \theta \cdot \sin^2 2\theta}{\sin 4\theta} \cdot \frac{dD}{2R}$$

Hence for a given change in D the proportionate change in the plane spacing d is proportional to the function $\frac{\cot \theta \cdot \sin^2 2\theta}{\sin 4\theta} = \frac{1 + \cos 2\theta}{2 \cos 2\theta}$, and by plotting the derived parameter for each line against this function, the true parameter can be obtained by extrapolation to $f(\theta) = 0$, i.e. $\theta = 90^\circ$, at which point the parameter is independent of the position of the sample.

FUNDAMENTAL CHARACTERISTICS OF CASTING FLUIDITY.* 1174

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SYNOPSIS.

An apparatus incorporating certain novel features of design was used to study the effects of the degree of superheat, mould temperature, composition of certain binary alloys, and modification of aluminium-silicon alloys on the casting fluidity. A straight-line relationship between fluidity and absolute temperature was found for a number of pure metals. Certain general and previously established relationships between the casting fluidity and the composition of binary alloys were confirmed for the lead-tin and aluminium-silicon systems. Modified aluminium-silicon alloys were found to possess lower fluidity than non-modified alloys. On the basis of the results obtained by these and additional tests, it is suggested that the variation of casting fluidity with temperature, in the case of pure metals, and with composition, in the case of binary alloys, can be explained in terms of certain properties of liquids, in particular the heat content and viscosity.

I.—INTRODUCTION.

THE nature of the flow of metallic liquids has been investigated in the past from two different aspects. Physicists have been mainly interested in the property of viscosity (its reciprocal value being defined as absolute fluidity), as one of the fundamental properties convenient for studying the nature of the liquid state and allied phenomena appertaining to liquids. Metallurgists, however, and in particular foundry metallurgists, have been more concerned with that property of a metallic liquid which enables it to fill a mould and to yield satisfactory cast products. Clearly, such a property, being a function of many variables, can be defined only on the basis of a suitable empirical test. Unfortunately, there is as yet no agreed or standardized method of evaluating this property, nor has the question of terminology been finally decided. In the following discussion, the word "fluidity" is used to mean this empirical property, i.e. casting fluidity, and not the reciprocal of viscosity.

That the viscosity of metals and alloys varies as a function of their state has long been recognized by physicists, just as metallurgists are

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aware that the same is true of the casting fluidity. Indeed, theoretical and experimental work has produced a number of well known and proved relationships in both fields. However, there still remain many unsolved problems concerning both these properties. The object of the present investigation, of which this paper constitutes the first report, is to clarify some of the outstanding points regarding casting fluidity, such as the effect of viscosity on the casting-fluidity values and the variation of casting fluidity with the composition, structure, and condition of liquid metals and alloys.

II.—PREVIOUS WORK AND SCOPE OF THE PRESENT INVESTIGATION.

1. *Viscosity.**

Certain aspects of the viscosity of metallic liquids, which are essential for the discussion, will be briefly reviewed, while those dealing with the question of casting fluidity will necessarily be considered in more detail.

Most of the current theories of the viscosity of liquids are based on experimental data obtained mainly from non-metallic liquids. However, as Andrade⁸ has shown, metallic liquids do not differ in respect of their viscous properties from other monomolecular liquids, and such well known relationships as, for example, the linear variation of the reciprocal of viscosity with absolute temperature, are also obeyed by metallic liquids.

From the point of view of the present investigation, the following two aspects of the viscosity of metals are of special interest: (a) the absolute viscosity of pure metals and alloys as a function of temperature above the melting points; (b) the variation of viscosity with concentration and constitution in simple binary systems. Unfortunately, owing to the considerable experimental difficulties involved in the absolute measurement of viscosity, only very scanty data on these two points are available. Viscosity values are known with a fair degree of accuracy for only a few low-melting-point metals, and not many measurements have been taken at temperatures close to the liquidus; moreover, the metals used have not always been of the highest purity. No detailed data are available on the relation of viscosity to the constitution of binary alloys, and such data as are available are controversial.

* A comprehensive list of references dealing with viscosity and the casting fluidity of metals has been published recently in a paper by K. L. Clark.¹ To avoid repetition, only those references not given in Clark's paper are added here.^{2, 3, 4, 5, 6, 7}

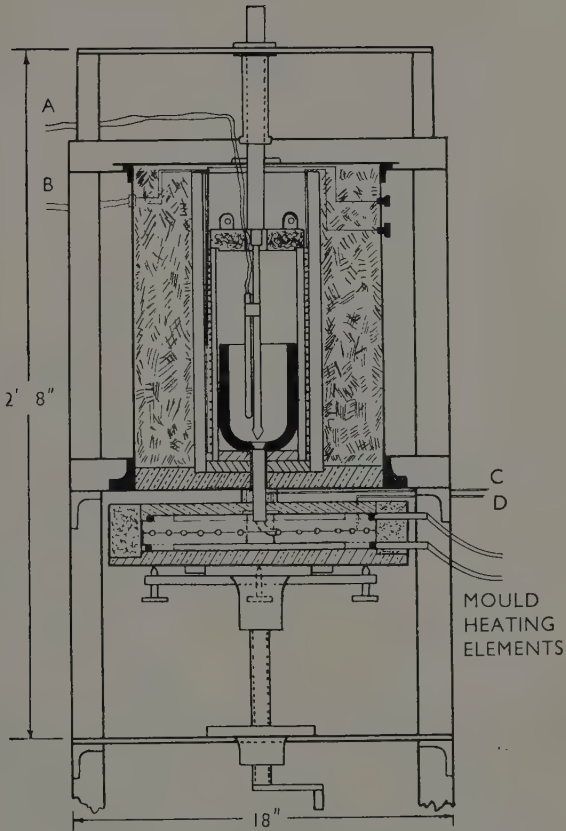


FIG. 1.—Fluidity Apparatus.



FIG. 2.—Cross-Section of the Fluidity Mould.

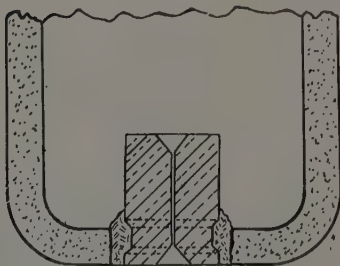


FIG. 3.—Rate-of-Flow Capillary.

2. Casting Fluidity.

Casting fluidity is normally measured by an empirical test in which the molten metal is made to run along a channel, usually of spiral form, in a horizontal mould made in sand or metal; the length of the resultant casting is defined as the casting-fluidity value. The main experimental variables of this test are the method of filling the mould (gating system), the type of mould, and the type of channel. Numerous designs of apparatus have been proposed and utilized, the main aim of the developments being towards increasing the accuracy and reproducibility of the results, and, at the same time, rendering the test of value in technological research as well as providing a quality production tool on the foundry floor. The principal features of the apparatus and the methods of determining the casting fluidity have been described by Clark ¹ and will not be elaborated here.

In spite of the variety of methods employed for obtaining fluidity values, a number of interesting results have been achieved which show that certain general relationships exist independently of the experimental techniques used. The more important of these are: (i) fluidity increases linearly with increasing temperature above the melting point; (ii) in a number of binary systems, fluidity first decreases with increasing percentage of solute and then increases again as the eutectic composition is approached; (iii) oxide films, dissolved gases, and impurities affect the fluidity values.

These and other data obtained by fluidity testing show that such measurements are sensitive enough to classify alloys in a certain order of increasing or decreasing fluidity, and can thus be useful in solving technological casting problems. On the other hand, it is very difficult on the basis of the available results to provide answers to such important questions as, for example: what fundamental properties of metallic liquids determine their casting fluidity? or, in other words: can the empirical value of the casting fluidity be interpreted theoretically?

The view generally held at present ⁹ can be summarized as follows: viscosity is a factor of only secondary importance in determining the casting fluidity of metals and alloys, while surface films, inclusions, mode of solidification, and mould properties are regarded as the prime factors. The experimental evidence available to support this view is, however, indirect and not strictly conclusive.

The problem then arises whether a more definite answer to the questions raised above can be found without resorting to the actual measurement of the physical properties involved. The view held by the present authors is that some purely physical measurements will

ultimately be necessary, but that much can still be learned by measuring the casting fluidity under conditions of full experimental control, a procedure which is not unduly difficult.

Accordingly, the first step taken in this experimental work was to carry a stage further the method of fluidity testing in current use, (a) by increasing the sensitivity of the apparatus, (b) by providing data which were still lacking, and (c) by checking some of the already known data under different conditions of testing.

3. *Design of the Apparatus.*

The main objections to existing methods of fluidity testing, from the point of view of research rather than production control, are as follows:

(a) Metal is transferred from a melting unit by pouring into the fluidity mould; this introduces the variables of turbulence and speed of flow, which are difficult to reproduce from test to test.

(b) The mould is normally used at room temperature, thus introducing a fast rate of cooling; under these conditions, the fluidity value is determined largely by the rate of heat transfer, so that the effects of physical properties such as viscosity are obscured. Moreover, in order to obtain reasonable lengths of spiral when low mould temperatures are used, fluidity tests have to be taken with metal temperatures well above the liquidus, and thus the very interesting range of fluidity values close to the liquidus cannot be investigated.

(c) Owing to objection (a) usually not more than one point resulting from a single test can be obtained under closely reproducible conditions; this reduces appreciably the over-all accuracy of the results, because a fair amount of scatter is inherent in the nature of the test.

An apparatus was designed (Fig. 1, Plate LXXXVIII) with the aim of overcoming the objections mentioned above. Melting is carried out in a resistance-wound electric furnace, the crucible being directly connected with the fluidity mould which is situated beneath the furnace. The mould, which is resistance heated, is made in two halves, and provides a $\frac{1}{4}$ -in.-dia. circular groove of an Archimedes spiral (Fig. 2, Plate LXXXIX). Cast iron or graphite moulds were used in the present series of experiments. A test is taken by displacing the plunger to allow the metal (held at the chosen temperature of super-heat) to run into the mould, the latter being held at its required temperature (see Figs. 4-9). Both metal and mould temperatures were controlled to $\pm 1^\circ$ C. Preliminary tests were carried out with the apparatus to ascertain the effects of any experimental variables likely to cause scattering of the results.

The apparatus can be used at a chosen hydrostatic pressure of the molten metal. It was important to check the effect of variation in hydrostatic pressure on the fluidity values, and the results obtained with tin are given in Fig. 4. These show that the hydrostatic pressure can be readily controlled to a sufficient degree to eliminate its effect on the fluidity values.

The second important experimental variable is the temperature of the mould. The relationship between the casting fluidity and mould temperature for commercially pure aluminium cast at 760°C . is shown in Fig. 5. It is seen that, at low mould temperatures, the fluidity is not sensitive to small variations, while at higher mould temperatures it becomes necessary to control the mould temperature to a considerable degree of accuracy.

The third important variable is the mould surface. Preliminary experiments showed that, by the application of colloidal graphite as mould dressing, a number of tests could be carried out without further treatment of the mould surface. Although this point still remains a

serious weakness of the apparatus for very accurate work, the results now described were not seriously affected through this cause. The experiments were carried out in air, but the apparatus can be readily adapted for controlled-atmosphere work.

III.—EXPERIMENTAL WORK AND RESULTS.

The following experiments were carried out :

(1) Fluidity values were obtained for some low-melting-point metals as functions of the molten-metal temperatures, at constant mould temperature and hydrostatic pressure.

(2) Fluidity measurements were carried out on alloys in the

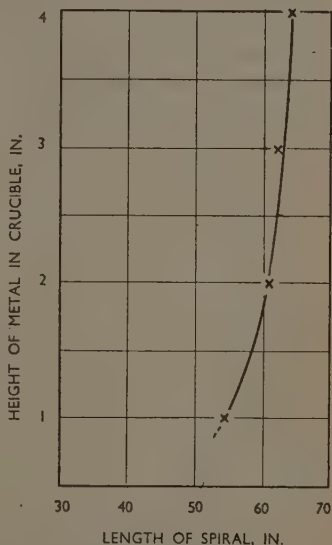


FIG. 4.—Effect of Hydrostatic Pressure on Casting Fluidity.

Metal temperature : liquidus $+ 25^{\circ}\text{C}$.
Mould temperature : liquidus $- 25^{\circ}\text{C}$.
Mould : cast iron.

lead-tin and aluminium-silicon binary systems, at constant pouring temperature above the liquidus for each alloy and constant mould temperature below the liquidus, and in all cases at constant hydrostatic pressure.

(3) Supplementary tests of a different nature (these are fully described later) were used to resolve certain questions raised in the first two series of tests.

In these experiments, tin, lead, cadmium, zinc, and aluminium of purity greater than 99.99%, and bismuth and silicon (99.90%) were

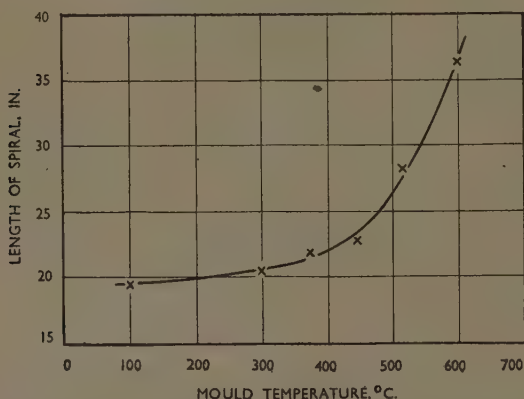


FIG. 5.—Effect of Mould Temperature on Casting Fluidity of Commercial-Purity Aluminium.

Metal temperature : 760° C.
Mould : cast iron.

used. In addition, the aluminium-silicon system was investigated with commercially pure (99.5%) metals. Necessary precautions were taken to prevent contamination of the very pure metals when melting and testing. In general, three tests were taken to obtain an average fluidity value for each point plotted on the graphs. The order of the scatter of results with the present apparatus was $\pm 2.5\%$.

The casting fluidities of cadmium, tin, and lead, as a function of casting temperature when cast into a mould held at 25° C. below their melting points, are shown in Fig. 6. In the same Figure the reciprocal of viscosity (i.e. absolute fluidity) as a function of temperature is plotted for tin, from viscosity data taken from Sauerwald's work.¹

The fluidity of lead-tin alloys was determined for a number of compositions sufficient to reveal the general character of the fluidity curves. The aluminium-silicon system was investigated up to 15% silicon. These results are given in Figs. 7-8. Fluidity graphs of commercially pure aluminium-silicon alloys were of the same type as those shown for very pure alloys.

In investigating a complex empirical property such as casting fluidity it becomes very difficult to apply the rule of measuring the effect of one variable at a time. The variables in this case are those related to: (a) the metal (heat content, density, surface tension, viscosity, crystallization characteristics); (b) the mould (thermal properties,

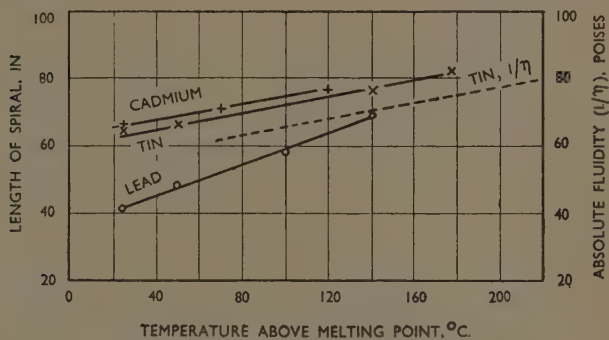


FIG. 6.—Effect of Temperature on Casting Fluidity.

Mould : cast iron.

surface characteristics); and (c) the experimental conditions (hydrostatic pressure, type of mould channel).

In the experiments described above, the problem of the selection and control of variables was resolved in the following way. In studying the effect of temperature, i.e. heat content, on fluidity, the mould and experimental conditions were kept constant so that the operating variables were, in this case, those of the metal. For the investigation of the fluidity of binary alloys, a comparison can be made of the fluidity of alloys of the same heat content. As the thermal properties of the alloys concerned were not available, it was decided to use a constant pouring temperature above the liquidus for each alloy, while the mould was held at a constant temperature below the liquidus. In this way, the rate of cooling was kept reasonably constant in any one series.

IV.—DISCUSSION OF RESULTS.

1. Fluidity of Pure Metals.

When fluidity values for pure metals are obtained under identical experimental conditions, the metals can be arranged in a series of in-

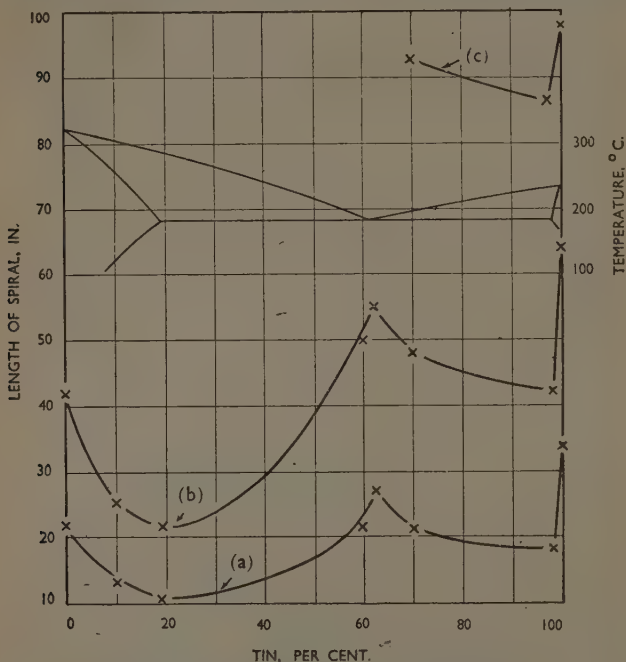


FIG. 7.—Casting Fluidity of Lead-Tin Alloys.

Metal temperature for all curves: liquidus + 25° C.

Mould temperature: curve (a) 100° C.

" (b) liquidus - 25° C.

" (c) liquidus - 6° C.

Mould: cast iron.

creasing fluidity values. The problem of casting a fluidity spiral being essentially one of heat extraction from the molten metal and of liquid flow, the two properties most likely to determine fluidity values are the heat of fusion per unit volume and the viscosity of the liquid metal. Values of these properties for the metals under investigation, taken

from the International Critical Tables, are given in Table I. Casting-fluidity values obtained in the present work are also included in this Table.

Three results show that, with the exception of bismuth, the arrange-

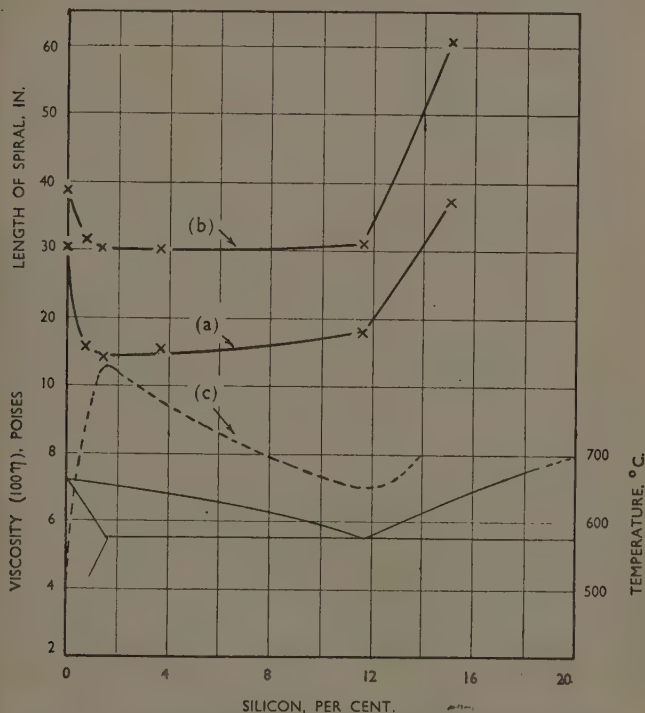


FIG. 8.—Casting Fluidity of Aluminium-Silicon Alloys of High Purity.

Metal temperature: curve (a) liquidus + 25° C.

„ (b) liquidus + 100° C.

Mould temperature: curves (a) and (b) liquidus - 100° C.

Mould: cast iron.

Curve (c) shows viscosity data (Polyak and Sergeev ¹²).

ment in order of increasing casting fluidity is the same as that in order of increasing heat of fusion per unit volume. (The position of bismuth is rather doubtful in view of the lower purity of this metal.) A different and less orderly sequence of fluidity values was obtained by Bastien,¹⁰

TABLE I.

	Lead	Bismuth	Tin	Cadmium	Zinc
Heat of Fusion, g.-cal./g. . .	5.9	12.0	14.5	13.0	24.4
Heat of Fusion per Unit Volume, g.-cal./c.c. . .	64.2	120.4	101.2	103.9	168.8
Absolute Fluidity at the Melting Point, $1/\eta$, poises . .	34.5	43.5	50	66.5	...
Casting Fluidity. (Metal temperature 25° C. above, mould temperature 25° C. below, melting point of metal) .	42	49	64	65	109

who, however, used a mould at room temperature. Such data of absolute fluidity as are available fall also into the same arrangement.

It is difficult to assess numerically the effects of either surface tension or of oxide films on the casting fluidity of the metals investigated, but the results obtained are not likely to be greatly affected by these factors. Bircumshaw's results¹¹ show, for example, that the surface tension of zinc is greater than that of the other metals in Table I, and yet zinc has the highest fluidity. With certain other metals, e.g. aluminium, and under certain casting conditions, such as turbulent flow, oxide films might, however, exert an important effect on the casting fluidity. This problem is being investigated.

At a constant mould temperature, the fluidity generally increases linearly with increasing metal temperature over a wide temperature range; a relationship also found by several other investigators. This relationship breaks down, however, under certain experimental conditions, e.g. when a low mould temperature is used. It is premature to speculate in detail at this stage on the significance of this linear relationship, but it is interesting to note that the absolute fluidity-metal temperature relationship is also a linear one, as shown for tin in Fig. 6.

2. Fluidity of Binary Alloys.

Numerous investigators report that the casting fluidity of binary alloys usually decreases with increasing solidification interval, and shows a maximum at compositions solidifying at a constant temperature. Such behaviour has been explained generally by the assumption that during a fluidity test the metal flows down the spiral through a thin shell of solid metal of the same composition, which forms on the mould wall owing to a steep temperature gradient; this shell, in the case of alloys having a long solidification interval, exerts a maximum retarding influence on the metal flow in a narrow channel. This

retarding influence is believed to be also dependent on the type of crystals formed during solidification.

Whereas a fluidity-composition behaviour of this nature has been confirmed in the present investigation for the lead-tin system, using moulds both at low and at high temperatures, the results obtained with the aluminium-silicon system show that there are exceptions to these rules, and such exceptions have also been found by other workers.

Two questions arise from these considerations: (1) are there any factors, other than those suggested above, which could account for a decrease in fluidity with increasing solidification interval? and (2) what factors could account for the exceptional behaviour of certain alloy systems?

Practically no data exist on the variation of heat of fusion with composition for binary systems. It is, however, difficult to believe that variation of this property could account for the general shape of the fluidity-composition curves.

Similarly, there are no reliable data available on the viscosity of binary alloys. While some investigators claim that viscosity graphs of binary systems do not show pronounced maxima or minima, others have found that the viscosity of a pure metal increases rapidly at first with the introduction of solute atoms and decreases again at higher compositions, showing a minimum at the eutectic composition. It is hoped to obtain a definite answer to this question by viscosity measurements planned as part of the present investigation. Certain preliminary experiments have already been carried out by comparing the rate of flow of binary lead-tin alloys through a capillary tube, by the method illustrated in Fig. 3 (Plate LXXXIX). Under conditions similar to those of the fluidity measurements, the volumes of alloys which flowed out through the capillary in 30 sec. at 6° C. above the liquidus were compared. A cast iron capillary tube, 0.04 in. in dia. and 1 in. long, was used. The results are shown in Table II, from which it is seen that

TABLE II.

	Percentage of Tin in Lead-Tin Alloy				
	0%	19.2%	61.9%	97.5%	100%
Rate of Efflux, c.c./30 sec.	11.68	10.0	11.4	10.5	13.88

alloys of maximum solubility flow more slowly than the pure metals or the eutectic alloy, even under conditions where restricting factors due to a thin crystal shell cannot operate.

More recently, Polyak and Sergeev¹² have obtained rather similar relationships for the viscosity values of aluminium-silicon alloys. Their results are included in the fluidity graphs in Fig. 8. Moreover, they showed that small additions of sodium raise appreciably the viscosity of the eutectic alloy. For this reason additional fluidity measurements were made by the present authors on the eutectic alloy, after adding 0.1% sodium at 735° C. The results (Fig. 9) show that fluidity is appre-

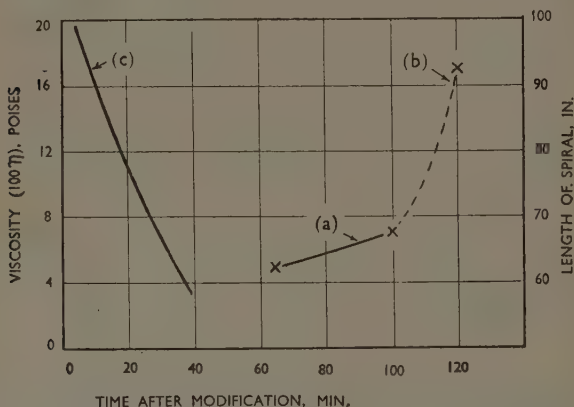


FIG. 9.—Effect of Modification on Casting Fluidity of Aluminium-Silicon Eutectic.

Metal temperature: liquidus + 70° C.
 Mould temperature: liquidus - 100° C.
 Mould: graphite.

Curve (a) before modification.
 " (b) after modification.
 " (c) viscosity data (Polyak and Sergeev¹²).

ciably reduced by modification with sodium, and can be completely restored by demodification.

On the basis of the above-quoted results, it is suggested that the fluidity-composition relationship of binary alloys is influenced mainly by changes in the properties of the liquid with composition, and that such factors as mechanical interference of growing dehdrites play only a secondary part in determining the general shape of the fluidity curves. It is to be expected, of course, that under suitable experimental conditions mechanical factors might introduce small alterations in the shape of the curves.

It is at present difficult to account for the increase of fluidity with

compositions higher than the eutectic in the aluminium-silicon system. According to Polyak and Sergeev, viscosity increases rather than decreases in this composition range. Against this, it should be noted that the heat of fusion of silicon (it is generally believed that silicon crystals form on solidification of these alloys) is unusually high (707 g.-cal./c.c.) which might counteract any rise in viscosity values.

V.—CONCLUSIONS.

Evidence has been obtained to show that two widely held views about casting fluidity: (1) that viscosity is of minor importance, and (2) that solid-solution alloys possess lower fluidity on account of their mode of solidification, will have to be reconsidered. In contradiction to these views it is suggested that the question of interpreting the casting fluidity test for many metals and alloys is essentially that of expressing fluidity in terms of other known and measurable properties of metallic liquids, in particular, the viscosity and heat content. The importance of oxide films in the case of some metals and alloys will have to be assessed from further experimental work. The present investigation, which was of an exploratory nature, shows also that it might be possible to establish a quantitative relationship between fluidity and other properties of a liquid, provided fluidity testing is carried out under suitable controlled conditions. As a corollary, it will also be necessary to carry out further measurements of viscosity and thermal properties of metallic liquids.

It is hoped that a more fundamental investigation of fluidity of this type will contribute not only to a better understanding of the liquid state but also to the interpretation and standardization of fluidity testing in its use for production control in the foundry.

ACKNOWLEDGEMENTS.

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THE CREEP STRENGTH AT 200° C. OF SOME 1175 MAGNESIUM ALLOYS CONTAINING CERIUM.*

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(Communication from the National Physical Laboratory.)

SYNOPSIS.

A number of alloys of magnesium containing cerium or "mischmetal" (a mixture of rare earth elements in which cerium predominates), with or without additions of manganese, were tested in creep at 200° C. under a stress of 2 tons/in.² in the conditions: (a) as cast, (b) as rolled, and (c) as rolled and heat-treated. It was found that under these particular conditions of testing little advantage is gained by increasing the cerium content beyond 1½ or 2%, and that rolled alloys are markedly inferior to cast alloys unless they are solution treated, when they become as strong as the cast material. Some slight age-hardening was found to take place in alloys containing from 0.5 to 6% of cerium, and the creep resistance appears to be associated with this phenomenon. Cerium in the form of a eutectic network, or as coarse particles precipitated at 250° C. or at higher temperatures, does not contribute to the strength of the alloy in creep at 200° C.

I.—INTRODUCTION.

THIS paper describes the first stage of an investigation of the factors underlying the superior creep resistance at elevated temperatures of magnesium alloys containing cerium.

The fact that alloys containing mixtures of rare earth metals (cerium, lanthanum, &c.) have valuable properties at elevated temperatures has been known for many years. Haughton and Prytherch¹ carried out a number of elevated-temperature tests on alloys containing rare earths together with calcium, nickel, manganese, and cobalt, and took out a patent² covering such alloys. The superiority at 150° C. of alloys AM6 (6% rare earths, 2% manganese) and AM537 (0.5% rare earths, 2% manganese) over the aluminium-containing alloys was shown by Beck.³ Many other investigators^{4, 5, 6, 7} have published the results of tensile, creep, and fatigue tests at temperatures up to 300° C. While such alloys are greatly superior to other known magnesium alloys in the temperature range 150°–200° C., they have relatively poor room-temperature properties. Murphy and Payne⁸ have shown that additions of zirconium enhance the room-temperature properties without any deleterious effect on the creep resistance at 200° C.

In the present work most of the alloys were made with additions of

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cerium rather than of mixtures of rare earth metals. Creep tests were carried out at 200° C. under a stress of 2 tons/in.² (3.15 kg./mm.²), and the materials were compared in terms of the total strain after 120 hr. and the rate of creep at 120 hr. The temperature of 200° C. is one which magnesium alloys may reach in some practical uses, and the stress of 2 tons/in.² is one which certain existing magnesium alloys, e.g. AM6, are able to carry at 200° C. without undergoing more than a few tenths of one per cent. elongation in the course of a reasonable service life, and therefore is one which could be applied in practice. In most of the tests the load was maintained for 150 hr. and a few tests were continued for 1000 hr. The test-pieces were 8½ in. (21.6 cm.) long × 0.564 in. (1.43 cm.) dia. in the parallel portion, with a gauge length of 5 in. (12.7 cm.). In a few cases it was necessary to use smaller test-pieces of 0.357 in. (0.91 cm.) dia. in the parallel portion and with a gauge length of 2 in. (5.1 cm.).

The earlier experiments were made on cast alloys, but it was later found to be more convenient to work with bars rolled from chill-cast ingots with an intermediate press forging operation.

While the bulk of the alloys were made with cerium of 98% purity, for purposes of comparison a number of alloys were also made with commercial "mischmetall", and in addition a number of alloys in which manganese was also present were examined. Magnesium of purity not less than 99.97% was used for all alloys.

II.—EXPERIMENTAL WORK.

1. *Reproducibility of Results.*

The behaviour of an alloy in creep tests is well known to be very sensitive to slight variations in its condition, and for this reason closely reproducible results are difficult to obtain. Two series of tests were used to assess the reproducibility attained in the present work. In one of these, eight similar test bars of an alloy containing 1.7% cerium were cast in one moulding box, so that all the bars were fed at the same time and at the same rate from one crucible of metal. Fig. 1 (Plate XC) shows the resulting casting with runners and risers. Six of the bars were subjected to creep tests as cast and gave the results shown in Table I.

In the second series, four test-piece lengths were cut from a hot-pressed and rolled bar of an alloy containing 1.71% of cerium and 0.25% of manganese. The bars were given identical solution treatment by heating for 24 hr. at 550° C. and quenching in water. The results of creep tests are given in Table II.

From these results it is seen that variations of 2 or 3 : 1 in single

TABLE I.—1.7%-Cerium Alloy, As Cast.

Reference No.	Strain at 120 hr., millionths	Creep Rate at 120 hr., millionths/hr.
X52B3 *	3000	14.7
X52B4 *	3580	17.7
X52B5	1570	8.0
X52B6	2060	13.1
X52B7	2600	14.4
X52B8	3970	21.7

* Small test-piece. ●

TABLE II.—1.71% Cerium, 0.25% Manganese Alloy, Heated 24 hr. at 550° C., Water Quenched.

Reference No.	Strain at 120 hr., millionths	Creep Rate at 120 hr., millionths/hr.
X72B1	31	0.11
X72B3	54	0.205
X72C1	40	0.23
X72C2	27	0.195

tests are not specially significant, and that considerable chance variation could occur in the mean results from duplicate tests. Most of the tests were carried out in duplicate and the mean results are used in the discussion and in Tables I-X. The full details are, however, given in Table XI for cast alloys, and in Table XII for rolled alloys.

2. Comparison of Effect of Additions of Cerium and of "Mischmetall".

Commercially, cerium is generally added to magnesium alloys in the form of a temper alloy made up with "mischmetall". To confirm that cerium contributes materially to the improvement of creep resistance obtained, tests were made on two series of alloys, in one of which the addition alloy containing 25% cerium was made from cerium of 98% purity, while the addition alloy for the other series was made from "mischmetall" and contained 25% rare earth elements. Typical analyses of the "mischmetall" and of the addition alloy were:

	"Mischmetall", %	Addition Alloy, %
Magnesium	75.35
Cerium	52.0	14.3
Lanthanum and other rare earths . .	46.6	10.0
Iron	1.26	0.11

The tests were made on sand-cast bars, cast horizontally in pairs and fed from one end. Melrasal fluxes Z and E were used for protection during melting and alloying, an allowance of 10% was made for loss of cerium in melting and casting, and the metal was poured at approximately 740° C. Radiographic examination showed that the bars cast in this way were sound.

Alloys with additions of cerium or of rare earths up to 6% were made and subjected to creep testing as cast. Table III summarizes the results. Certain industrially produced creep-resisting magnesium alloys tested under the same conditions showed strains of 80–600 millionths in 120 hr. and creep rates of 0.4–4 millionths/hr. at 120 hr. Under the conditions of testing, i.e. 2 tons/in.² (3.15 kg./mm.²) at 200° C., the same order of creep resistance can be reached by the simple addition of as little as 1.3% cerium, and 6.0% cerium does not effect a great improvement. This standard is not attained consistently, particularly when the cerium content is below 3.0%. The creep resistance is generally of the same order when "mischmetall" is used instead of cerium, but the results with "mischmetall" are more consistent and the alloys are rather stronger.

TABLE III.—*Comparison of Alloys Made with Cerium and with "Mischmetall".*

Reference No.	Composition	Average Strain at 120 hr., millionths	Average Creep Rate at 120 hr., millionths/hr.	Number of Tests
(a) Additions of "Mischmetall"				
X19	0.47% rare earths	5750	39	2
X20	1.0 "	1340	3.7	4
X17	1.6 "	1050	2.95	3
X18	1.62 "	260	0.71	2
X11	3.4 "	240	0.66	2
X32	5.4 "	97	0.31	2
(b) Additions of Cerium				
X45	1.3% cerium	560	1.77	2
X22	1.4 "	2500	11.8	1
X52 *	1.7 "	2797	14.9	6
X46	3.5 "	355	0.68	2
X59	4.1 "	692	1.66	2
X38	6.0 "	590	2.07	3
X55	6.0 "	350	0.88	2

* 8 bars cast together as illustrated in Fig. 1 (X52B1–X52B8).

The experiment will bear the interpretation that the creep resistance is due essentially to the influence of a rather low proportion of cerium



FIG. 1.—Casting of Eight Test-Pieces.

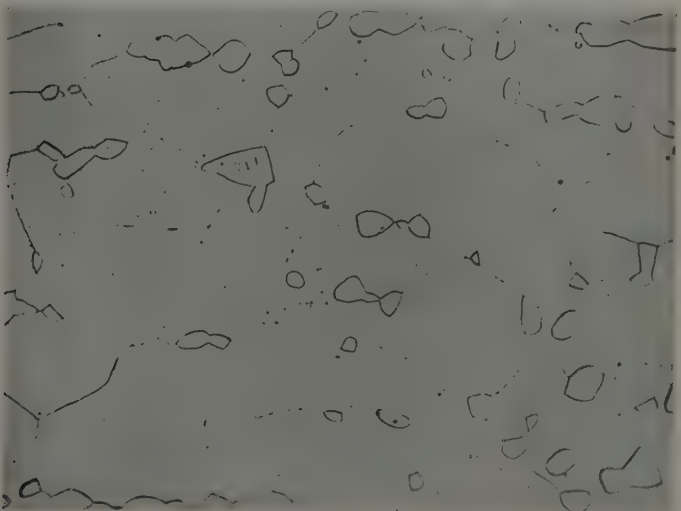


FIG. 2.—Alloy X62 (4.33% Cerium), Solution Treated 24 hr. at 580° C. and Water Quenched. $\times 500$.

[To face p. 682.]

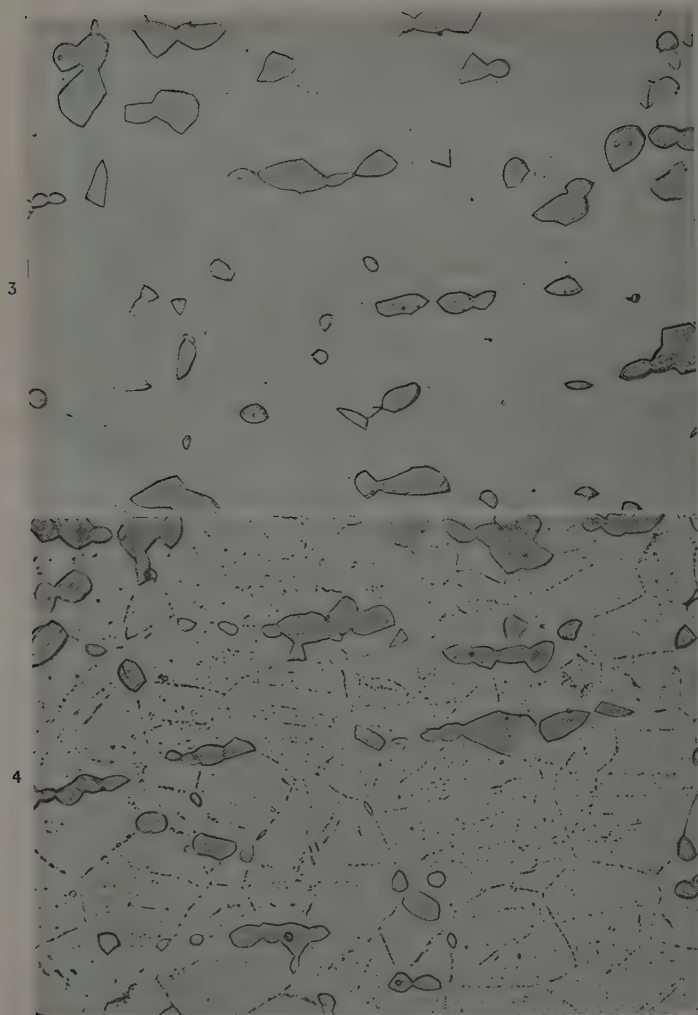


FIG. 3.—Alloy X62 (4.33% Cerium), Solution Treated and Aged 16 hr. at 200° C. $\times 500$.

FIG. 4.—Alloy X62 (4.33% Cerium), Solution Treated and Aged 16 hr. at 350° C. $\times 500$.

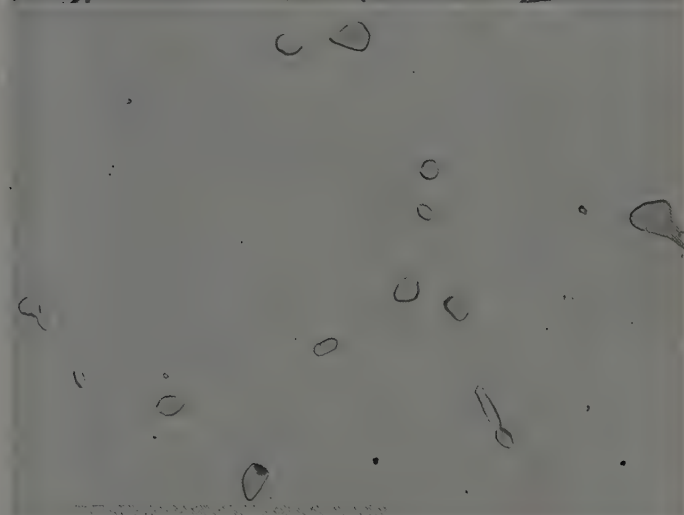
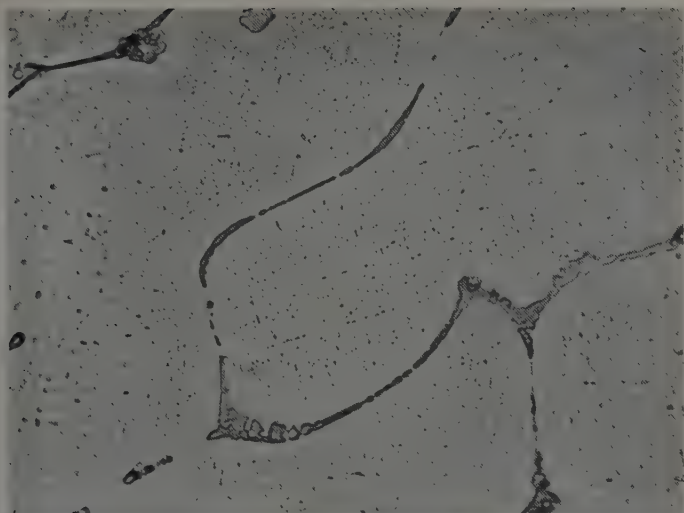


FIG. 5.—Alloy X17 (1.6% Rare Earths), Cast and Annealed 2 hr. at 350° C.
× 500.

FIG. 6.—Alloy X17 (1.6% Rare Earths), Cast and Solution Treated 24 hr. at
550° C. × 500.

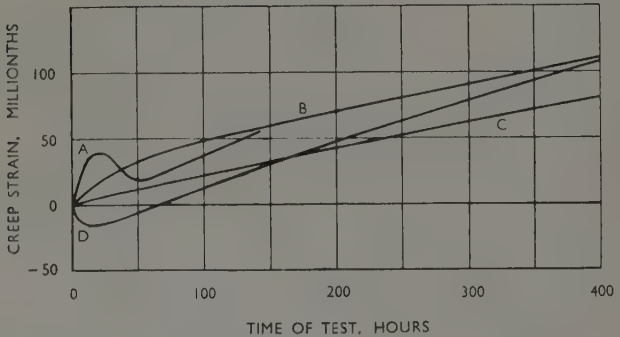


FIG. 7.—Creep Curves of Two Alloys Tested at 200° C., 2 tons/in.²

KEY.

- A. X64C2 held 18 hr. at 200° C. before loading.
- B. X72C1.
- C. X72C2.
- D. X64C1 held 50 hr. at 200° C. before loading.

X64: 6% rare earths, 1.5% manganese; 24 hr. at 580° C. and water quenched.

X72: 1.7% cerium, 0.25% manganese; 24 hr. at 550° C. and water quenched.

(about 1.5%), but that the cerium is not always in a form which gives maximum creep resistance, and good creep resistance cannot be relied on unless the cerium content is somewhat higher. The required form seems to be more frequently obtained in the less-pure alloys made with "mischmetall".

The results of a few experiments on the heat-treatment of castings are recorded in Table XI (p. 689). They show that annealing at 350° C. lowers the creep resistance of cast alloys, and that a solution treatment of 24 hr. at 550° C., followed by water quenching, does not effect any consistent improvement.

3. Wrought Alloys Made with Cerium (98% Purity).

Further experiments were carried out on wrought alloys made with 98% cerium, and in these the influence of heat-treatment was investigated. Alloys were cast into 2¼ in. (5.7 cm.) square chill moulds, press forged from 500° C. to 1½ in. (3.8 cm.) dia., and rolled from 500° C. to 1⅝ in. (2.4 cm.) dia. Blanks 8½ in. (21.6 cm.) long were heat-treated, and creep test-pieces were subsequently machined from them. The melting procedure and casting temperature were the same as for the cast alloys.

(a) Alloys Tested As Rolled.

Table IV is a summary of the results of tests made on the bars as rolled. In this condition, the creep rates were all high, in general much higher than those of corresponding cast alloys and, although the strength was greater than that of pure magnesium (see alloy X75A in Table V),

TABLE IV.—*As-Rolled Magnesium-Cerium Alloys.*

Reference No.	Cerium Content, %	Average Strain at 120 hr., millionths	Average Creep Rate at 120 hr., millionths/hr.	Number of Tests
X66B	0.48	5,600	34	2
X61B	1.45	1,500	19.7	2
X69C	2.55	9,000	65	1
X67B	3.8	10,000	high *	1
X62B	4.33	3,870	31.2	2
X63B	5.95	8,350	69.5	2
X55A	6.0	15,600	95	1

* Test discontinued before 120 hr.

addition of further cerium beyond the first half per cent. produced no consistent improvement. The figures suggested that the precise conditions of rolling might have more effect on the behaviour than the total cerium content.

(b) *Alloys Tested as Solution Treated at 550° or 580° C.*

When the rolled alloys were quenched in water after being heated for 24 hr. at 550° or 580° C., the creep resistance was much improved and became of the same order as, and on the whole rather better than, that of cast alloys of equal cerium content (Table V). The alloys

TABLE V.—*Rolled Magnesium-Cerium Alloys, Tested as Water Quenched from 550° or 580° C.*

Reference No.	Cerium Content, %	Average Strain at 120 hr., millionths	Average Creep Rate at 120 hr., millionths/hr.	Number of Tests
(a) 24 hr. at 550° C., Water Quenched				
X75A	0	Broke in less than 200 min.		2
X76A	0.19	"	"	2
X66B	0.48	1060	1.53	2
X61B	1.45	260	1.35	2
X52A	1.7	112	0.65	2
X69E	2.55	82	0.4	2
X67C	3.80	175	0.65	1
X62B	4.33	255	1.00	2
X63B	5.95	274	1.02	2
(b) 24 hr. at 580° C., Water Quenched				
X66C	0.48	127	0.20	2
X61B	1.45	66	0.23	1
X69C	2.55	147	0.57	1
X67B	3.80	230	0.79	2
X62C	4.33	158	0.50	1
X63B	5.95	207	0.56	2

quenched from 550° C. improved rapidly as the cerium content increased from 0 to about 2% and thereafter changed little. The creep strength of alloys quenched from 580° C. was on the whole better than that of alloys quenched from 550° C., particularly in alloys of lower cerium content. The most interesting result in this series is that on the 0.48%-cerium alloy, which when water quenched from 580° C. behaved almost as well as any of the alloys of greater cerium content. It was usual to maintain the test-pieces for 16 hr. at the test temperature in order to attain uniform conditions before applying the load, so that the condition of the material when the load was applied might perhaps be better described as "solution treated, water quenched, and aged 16 hr. at 200° C." than as "water quenched".

(c) *Effect of Ageing at Various Temperatures.*

Ageing for 16 hr. at 150° C. made little difference to the results, as may be seen by comparing Table VI with Table V(a), but ageing at

temperatures above 200° C. caused a loss in creep strength which is illustrated by the figures for the 1.45%-cerium alloy in Table VII. The improvement secured by heat-treatment was entirely lost by ageing at 350° C., but some alloys, e.g. the 4.33%-cerium alloy, appeared to be able to withstand heating to 250° C. without serious loss of properties.

TABLE VI.—*Rolled Magnesium-Cerium Alloys, Water Quenched After 24 hr. at 550° C., and Reheated 16 hr. at 150° C.*

Reference No.	Cerium Content, %	Average Strain at 120 hr., millionths	Average Creep Rate at 120 hr., millionths/hr.	Number of Tests
X66B	0.48	755	0.5	1
X61C	1.45	110	0.52	2
X69C	2.55	266	0.92	2
X67B	3.8	178	0.65	1
X62C	4.33	151	0.81	2
X63C	5.95	382	1.50	2

TABLE VII.—*Effect of Reheating on 1.45%-Cerium Alloy, Water Quenched After 24 hr. at 550° C.*

Reheating Treatment	Average Strain at 120 hr., millionths	Average Creep Rate at 120 hr., millionths/hr.	Number of Tests
None	260	1.35	2
16 hr. at 150° C.	110	0.52	2
16 hr. at 265° C.	676	2.14	3
16 hr. at 350° C.	7550	55	2

(d) *Age-Hardening and Microstructure.*

The general effects of solution and ageing treatments suggest that the creep strength of these alloys is essentially due to the retention of cerium in solution with some form of precipitation before or during test at 200° C. According to Haughton and Schofield⁹ the solid solubility of cerium in magnesium falls from 1.6% at the eutectic temperature of 590° C. to less than 0.1% at 400° C., and age-hardening phenomena are therefore possible. Table VIII records the results of age-hardening tests on some rolled magnesium-cerium alloys. The alloys harden, but only to a slight extent. It is noticeable, however, that the hardening first appears at the cerium content at which useful creep strength begins to be found (0.48%), and that the ageing temperature of 350° C. at which the improvement of creep resistance is lost is also one at which little or no hardening occurs. The creep resistance appears to be associated with a stage in the precipitation process rather than with the actual hardness of the alloy, since the 0.48%-cerium alloy, which had a diamond

pyramid hardness of about 40, had much the same creep resistance as the 4.33%-cerium alloy, which was some 15-20 points harder.

TABLE VIII.—*Precipitation-Hardening Tests on Rolled Magnesium-Cerium Alloys.*

Reference No.	Cerium Content, %	Temp. of Solution Treatment, °C.	Temp. of Ageing, °C.	Brinell Hardness (5 mm./125 kg./15 sec.) After Ageing				
				0 hr.	2 hr.	4 hr.	16 hr.	88 hr.
X75	0	580°	150°	27.8 *	27.6 *	...
			200°	30.7 *	...
X76	0.19	580°	150°	31.2	30.0	31.8	32.1	32.1
			200°	...	32.4	33.8	32.8	30.6
X66	0.48	580°	150°	36.2	39.9	...
			200°	41.4	...
X61	1.45	580°	150°	40.0	46.3	47.2	48.7	49.7
			200°	...	51.6	49.1	47.2	46.9
			250°	...	46.7	46.8	46.4	46.3
			350°	...	42.5	42.5	40.6	38.6
X62	4.33	580°	150°	51.0	54.0	55.3	59.8	55.7
			200°	...	55.3	56.3	60.3	52.1
			250°	...	51.7	52.1	56.1	49.4
			350°	...	48.5	47.5	49.7	45.0
X73	1.76% rare earths	580°	150°	41.9	45.5	47.0	52.2	48.9
			200°	...	49.4	49.7	51.4	45.5
			250°	...	46.5	46.0	49.3	43.8
			350°	...	43.0	41.8	44.4	38.9

* Diamond pyramid hardness numbers.

Included in Table VIII are some results on an alloy made with "mischmetall", and containing 1.76% of rare earths. Its behaviour was similar to that of alloys made up with cerium.

Figs. 2-4 (Plates XC and XCI) show the microstructures of the 4.33%-cerium alloy as quenched from 580° C., quenched and aged at 200° C., and quenched and aged at 350° C., respectively. A fine precipitate is visible in the sample aged at 350° C., which after this treatment would have low creep resistance, but no precipitate is visible in the alloy aged at 200° C., which has high creep resistance. The network of magnesium-cerium compound that is present in cast alloys appears to have little influence on the creep resistance. Fig. 5 (Plate XCII) shows the network in a cast alloy which had poor creep resistance after annealing for 2 hr. at 350° C., while Fig. 6 (Plate XCII) shows the same alloy with the network largely dissolved, but nevertheless with good creep resistance.

4. Alloys Containing Manganese.

A number of cast alloys with additions of 0.44–1.6% of manganese as well as of “mischmetall” were examined. The data are given in Table IX, and if these are compared with the corresponding manganese-free series in Table III, it is seen that the manganese-containing alloys are on the whole a little better.

TABLE IX.—*Cast Manganese-Containing Alloys Made with “Mischmetall”.*

Reference No.	Composition, %		Average Strain at 120 hr., millionths	Average Creep Rate at 120 hr., millionths/hr.	Number of Tests
	Rare Earths	Manganese			
X16	1.6	1.6	400	0.62	1
X24	3.73	1.4	125	0.66	2
X39	3.97	0.44	46	0.18	4
X31	5.0	1.2	150	0.72	2
X64	6.14	1.54	70	0.38	2

A few rolled alloys containing similar quantities of manganese also gave slightly better results than corresponding manganese-free alloys (see Table XII). Manganese-containing alloys may give complex creep curves which show a contraction either immediately after loading or after the test has continued for some hours (Fig. 7, Plate XCIII). The time of holding at the testing temperature prior to loading exerts an influence, and it would appear that some additional form of precipitation occurs when manganese is present.

It is doubtful whether any increased creep resistance due to manganese would be effective after the first 150 hr. of test.

5. Long-Time Creep Tests on Rolled Alloys at 200° C., 2 tons/in.² (3.15 kg./mm.²).

Since the creep resistance of the cerium alloys is associated with an ageing phenomenon, the possibility exists that in course of time over-ageing will occur, and the creep resistance be lost. For this reason several tests were continued for 300 hr., and some for 1000 hr. Within these times, there was no indication of any deterioration, the creep rates decreasing progressively as time went on (Table X). The indications, therefore, are that alloys of this kind would have useful service lives, though only more extended tests would show how long these lives would be.

TABLE X.—*Long-Time Creep Tests at 200° C., 2 tons/in.² (3.15 kg./mm.²).*

Reference No.	Composition, %			Condition.	At 120 hr.		At 300 hr.		At 1000 hr.	
	Ce	Rare Earths	Mn		Strain, millionths	Creep Rate, millionths/hr.	Strain, millionths	Creep Rate, millionths/hr.	Strain, millionths	Creep Rate, millionths/hr.
X66B7	0.48	As rolled	5,700	31	12,500	38
X66B4	0.48	24 hr. at 580° C., water quenched	121	0.37	214	0.43
X78B2	0.58	...	1.52	24 hr. at 580° C., water quenched	30	0.45	120	0.48	395	0.36
X72C1	1.71	...	0.25	24 hr. at 550° C., water quenched	40	0.21	90	0.21	240	0.18
X72C2	1.71	...	0.25	24 hr. at 550° C., water quenched	27	0.20	63	0.19	172	0.17
X69C2	2.55	24 hr. at 580° C., water quenched	147	0.57	210	0.20
X69C6	2.55	24 hr. at 550° C., water quenched, 16 hr. at 150° C., air cooled	262	0.87	385	0.60
X62C3	4.33	24 hr. at 550° C., water quenched, 16 hr. at 150° C., air cooled	152	0.76	250	0.50
X63C4	5.95	24 hr. at 550° C., water quenched, 16 hr. at 150° C., air cooled	335	1.09	530	0.80
X64C1	...	6.14	1.54	24 hr. at 580° C., water quenched	40	0.40	80	0.30

TABLE XI.—Cast Alloys Tested in Creep at 200° C., 2 tons/in.²
(3.15 kg./mm.²).

Reference No.	Composition, %			Treatment	Strain at 120 hr., millionths	Rate of Creep at 120 hr., millionths/hr.
	Rare Earths	Ce	Mn			
X19A1	0.47	As cast	3000	28
X19A2	0.47	As cast	8500	50
X20A1	1.0	As cast	1200	2.4
X20B1	1.0	As cast	2100	7.7
X20C1	1.0	As cast	920	1.8
X20D1	1.0	As cast	1140	2.8
X45A1	...	1.3	...	As cast	450	1.5
X45A2	...	1.3	...	As cast	670	2.05
X22C2	...	1.4	...	As cast	3500	11.8
X16D1	1.6	...	1.6	As cast	400	0.62
X17A1	1.6	As cast	510	2.15
X17C1	1.6	As cast	440	1.7
X17D1	1.6	As cast	2200	5.0
X17D2	1.6	2 hr. at 350° C.	8400	10.0
X17B1	1.6	24 hr. at 550° C., water quenched	770	2.8
X17B2	1.6	24 hr. at 550° C., water quenched	1000	3.3
X17C2	1.6	24 hr. at 550° C., water quenched, + 16 hr. at 350° C.	4600	14
X18A1	1.62	As cast	180	0.47
X18D1	1.62	As cast	840	0.96
X18D2	1.62	2 hr. at 350° C.	2300	8.0
X18B2	1.62	2 hr. at 350° C.	1640	3.6
X18B1	1.62	24 hr. at 550° C., water quenched	450	1.4
X18A2	1.62	24 hr. at 550° C., water quenched,	410	0.96
X18C2	1.62	+ 16 hr. at 350° C.	1650	9.2
X52B3 *	...	1.7	...	As cast	3000	14.7
X52B4 *	...	1.7	...	As cast	3580	17.7
X52B5	...	1.7	...	As cast	1570	8.0
X52B6	...	1.7	...	As cast	2060	13.1
X52B7	...	1.7	...	As cast	2600	14.4
X52B8	...	1.7	...	As cast	3970	21.7
X52B1	...	1.7	...	24 hr. at 550° C., water quenched,	1680	4.2
X52B2	...	1.7	...	+ 16 hr. at 250° C.	1220	2.8
X11C4	3.4	As cast	270	0.96
X11C6	3.4	As cast	210	0.35
X46A2	...	3.5	...	As cast	260	0.6
X46B1	...	3.5	...	As cast	450	0.76
X24A1	3.73	...	1.4	As cast	150	0.79
X24C1	3.73	...	1.4	As cast	100	0.54
X39A1	3.97	...	0.44	As cast	52	0.30
X39B1	3.97	...	0.44	As cast	110	0.10
X39A2	3.97	...	0.44	As cast	10	0.23
X39B2	3.97	...	0.44	As cast	14	0.10
X59B1	...	4.1	...	As cast	675	1.57
X59B2	...	4.1	...	As cast	710	1.75
X31A1	5.0	...	1.2	As cast	145	0.56
X31C1	5.0	...	1.2	As cast	165	0.87
X32C1	5.4	As cast	100	0.26
X32D1	5.4	As cast	94	0.36
X38A1	...	6.0	...	As cast	640	2.6
X38B1	...	6.0	...	As cast	720	2.3
X38C1	...	6.0	...	As cast	410	1.3
X55B1	...	6.0	...	As cast	380	0.82
X55B2	...	6.0	...	As cast	320	0.93
X64D1	6.14	...	1.54	As cast	77	0.4
X64E1	6.14	...	1.54	As cast	63	0.36

* Small test pieces

TABLE XII.—*Rolled Alloys Tested in Creep at 200° C., 2 tons/in.² (3.15 kg./mm.²).*

Reference No.	Composition, %			Treatment	Strain at 120 hr., millionths	Rate of Creep at 120 hr., millionths/ hr.	Remarks
	Rare Earths	Ce	Mn				
X75A1	24 hr. at 550° C., water quenched	Broke in 32 min.	...	17.5% elongation
X75A2	24 hr. at 550° C., water quenched	Broke in 200 min.	...	75% elongation
X76A1	...	0.19	...	24 hr. at 550° C., water quenched	Broke in 165 min.	...	15% elongation
X76A2	...	0.19	...	24 hr. at 550° C., water quenched	Broke in 128 min.	...	10% elongation
X66B1	...	0.43	...	As rolled	5,500	37	
X66B7	...	0.43	...	As rolled	5,700	31	
X66B2	...	0.43	...	24 hr. at 550° C., water quenched	1,020	1.52	
X66B3	...	0.48	...	24 hr. at 550° C., water quenched	1,100	1.65	
X66C1	...	0.48	...	24 hr. at 580° C., water quenched	85	0.16	
X66C2	...	0.48	...	24 hr. at 580° C., water quenched	170	0.25	
X66B5	...	0.43	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	765	0.5	
X78B1	...	0.58	1.52	24 hr. at 580° C., water quenched	70	0.32	
X78B2	...	0.58	1.52	24 hr. at 580° C., water quenched	30	0.45	
X61B1	...	1.45	...	As rolled	1,700	19.7	
X61B2	...	1.45	...	As rolled	1,300	...	
X61B3	...	1.45	...	24 hr. at 550° C., water quenched	270	1.4	
X61B4	...	1.45	...	24 hr. at 550° C., water quenched	250	1.3	
X61B5	...	1.45	...	24 hr. at 580° C., water quenched	66	0.23	
X61C4	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 550° C.	8,000	60	Small test-piece
X61C6	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 550° C.	7,100	80	Small test-piece
X61C1 (a)	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 295° C.	900	2.66	Small test-piece
X61C2 (a)	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 295° C.	655	2.0	Small test-piece
X61C2 (b)	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 295° C.	475	1.77	Small test-piece
X61C3 (a)	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	120	0.2	Small test-piece
X61C3 (b)	...	1.45	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	100	0.85	Held 3 hr. at 200° C. before test
X61B6	...	1.45	...	24 hr. at 580° C., water quenched + 16 hr. at 150° C.	66	0.23	Small test-piece
X52A1	...	1.7	...	24 hr. at 550° C., water quenched	50	0.6	Small test-piece
X52A2	...	1.7	...	24 hr. at 550° C., water quenched	175	0.7	Small test-piece

X72B1	1-71	0-25	24 hr. at 550° C., water quenched	31	0-11	
X72B3	1-71	0-25	24 hr. at 550° C., water quenched	54	0-205	
X72C1	1-71	0-25	24 hr. at 550° C., water quenched	40	0-23	
X73C1	1-71	0-25	24 hr. at 550° C., water quenched	27	0-195	
X69C1	2-55	...	As rolled	9,000	65	Held 48 hr. at 200° C. before test
X69E1	2-55	...	24 hr. at 550° C., water quenched	90	0-4	
X69E2	2-55	...	24 hr. at 550° C., water quenched	76	0-4	
X69C2	2-55	...	24 hr. at 580° C., water quenched	147	0-57	
X69C5	2-55	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	270	0-97	
X69C6	2-55	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	262	0-87	Held 3 hr. at 300° C. before test
X67B1	3-8	...	As rolled	>10,000	...	
X67C2	3-8	...	24 hr. at 550° C., water quenched	175	0-65	
X67B2	3-8	...	24 hr. at 580° C., water quenched	260	0-80	
X67B3	3-8	...	24 hr. at 580° C., water quenched	200	0-68	
X67B7	3-8	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	178	0-65	
X62B5	4-33	...	As rolled	3,340	31-4	
X62B6	4-33	...	As rolled	4,400	31-0	
X62B1	4-33	...	24 hr. at 550° C., water quenched	180	0-6	
X62B2	4-33	...	24 hr. at 550° C., water quenched	330	1-39	Held 3 hr. at 300° C. before test
X62C7	4-33	...	24 hr. at 580° C., water quenched	158	0-5	Held 26 hr. at 200° C. before test
X63C1	4-33	...	24 hr. at 550° C., water quenched + 16 hr. at 250° C.	205	0-75	
X63C2	4-33	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	215	0-61	
X62C3	4-33	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	152	0-76	
X62C4	4-33	...	24 hr. at 580° C., water quenched + 16 hr. at 150° C.	150	0-87	
X62C8	4-33	...	24 hr. at 580° C., water quenched + 16 hr. at 150° C.	177	0-37	
X63B3	5-95	...	As rolled	8,700	69	
X63B4	5-95	...	As rolled	8,000	70	
X63B1	5-95	...	24 hr. at 550° C., water quenched	154	0-69	
X63B2	5-95	...	24 hr. at 550° C., water quenched	395	1-36	
X63B6	5-95	...	24 hr. at 880° C., water quenched	155	0-545	
X63B7	5-95	...	24 hr. at 880° C., water quenched	260	0-57	
X63C1	5-95	...	24 hr. at 550° C., water quenched + 16 hr. at 250° C.	560	3-05	
X63C2	5-95	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	650	3-2	
X63C3	5-95	...	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	430	1-81	
X63C4	5-95	...	24 hr. at 580° C., water quenched + 16 hr. at 150° C.	335	1-09	
X63B8	5-95	...	24 hr. at 580° C., water quenched + 16 hr. at 150° C.	170	0-47	
X55A1	6-0	...	As rolled	15,600	95	
X64B1	6-14	1-54	As rolled	1,620	8-9	Held 41 hr. at 200° C. before test
X64B2	6-14	1-54	24 hr. at 550° C., water quenched	107	0-41	Held 50 hr. at 200° C. before test
X64C1	6-14	1-54	24 hr. at 580° C., water quenched	40	0-40	
X64C2	6-14	1-54	24 hr. at 580° C., water quenched	45	0-40	
X64B6	6-14	1-54	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	100	0-3	
X64B7	6-14	1-54	24 hr. at 550° C., water quenched + 16 hr. at 150° C.	70	0-42	

III.—DISCUSSION.

The general effect of these tests is to suggest that under the conditions of test employed, the increase in creep resistance brought about by additions of cerium is due principally to the first 0.5–1.5% of cerium that is taken into solid solution in the magnesium, and possibly precipitated in suitable form. In cast alloys, an excess of cerium appears to be desirable to ensure that about 1.5% is in solution throughout the alloy. The magnesium–cerium alloys, as is well known, have a low proof stress. For example, an alloy with 1.71% cerium and 0.25% manganese in the creep-resistant condition, i.e. rolled and solution treated, has a 0.1% proof stress of about 5.7 tons/in.² (8.97 kg./mm.²) at room temperature, associated with an ultimate tensile stress of 12.4 tons/in.² (19.5 kg./mm.²) and an elongation on $4\sqrt{\text{area}}$ of 13%. These properties are probably adequate for the stress that would be applied under conditions where creep strength is important, but if for any reason higher proof stress is required, it is probably better gained by other means than by addition of more cerium.

The decrease in creep resistance found after ageing at 250° and 350° C. indicates that binary magnesium–cerium alloys are not likely to maintain useful creep strength at temperatures higher than 250° C. Additions of third elements may, however, modify the solution and precipitation phenomena at 250° and 350° C., and extend the range of usefulness of the alloys.

ACKNOWLEDGEMENT.

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MECHANISM OF CREEP IN METALS.*

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SYNOPSIS.

It is shown how the mechanism by which a metal deforms at elevated temperatures differs from that operating at normal temperature, and how the difference depends on the rate at which the deformation takes place. At normal temperature deformation occurs mainly by the familiar mechanism of slip and the breakdown of the grains to crystallites of sub-microscopic size. As the temperature is raised and the rate of deformation diminished, this mechanism is increasingly replaced by one in which the grains dissociate into comparatively coarse units and permit flow by the relative movement of these units within the parent grains. The units, which are termed "cells", can be observed and measured. They are considered to be responsible for the continuous deformation under stress which characterizes the phenomenon of creep.

I.—INTRODUCTION.

THE present paper describes some observations on the mechanism by which a metal deforms when subjected to stress at elevated temperatures. It shows how the mode of deformation differs from that at normal temperature, and how the difference depends on the rate at which the deformation takes place.

A metal under stress as the temperature is raised tends to develop the slow continued deformation which has become known as "creep", and which forms the major problem in the development of alloys for use at high temperatures. The results now described, therefore, are related to this problem, and it is convenient first to refer to the two principal features already established in work on the mechanism of creep. Attention is confined throughout to deformations and to temperatures sufficiently below the melting point for the behaviour of the metals not to be complicated by recrystallization.

The first feature, discovered by Andrade,¹ is that creep may be analysed into two components. One is a deformation which begins at a relatively high rate as the stress is applied, but then dies away; the rate of deformation finally vanishing after a time depending on stress and temperature. The other is a superposed deformation which continues at a constant rate until the stage of fracture. This rate, usually termed the "minimum creep rate", again depends on stress and temperature; it is negligible at normal temperature and very low stresses, but assumes over-riding importance as the temperature is raised. These com-

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ponents have been aptly described in a recent paper by Orowan² as "transient" and "quasi-viscous" creep, respectively.

The second feature is that the two types of deformation are physically distinct. One proof of this point was obtained by Hanson and Wheeler³ from an elegant metallographic study of mechanically polished specimens of aluminium stressed at various temperatures. At normal temperature, with the transient component as main factor, deformation of the grains occurred by the familiar process of slip. But at higher temperatures, when the quasi-viscous component was the operative factor, the characteristic slip lines were no longer observed on the surfaces of the grains; instead the grain boundaries became emphasized by an apparent thickening. Hanson and Wheeler, therefore, described this latter creep process by the term "slip-less flow". Whether the slip lines were really absent, or whether they were on too fine a scale to be visible by the microscope, was uncertain; but the difference observed in the mode of deformation was of obvious significance. A second proof of a difference in mechanism was obtained more recently by Wood and Tapsell⁴ using X-ray diffraction. Plastic deformation of a polycrystalline metal at normal temperature breaks down the grains to sub-microscopic crystallites of varying orientation. Wood and Tapsell showed that this fine breakdown did not occur in slow deformation of aluminium specimens at sufficiently elevated temperatures, but instead the grains tended to preserve their entity. Whether they did so by a process resembling recrystallization or growth of the crystallites was not clear; it was evident, however, that at the higher temperature the normal mode of plastic deformation was different or profoundly modified.

Consideration of the above-described observations suggested that more definite information would follow from a correlated metallographic and X-ray study on identical specimens, and this approach has been followed in the present investigation, with results which could not have been obtained by either method alone.

Perhaps the main result is the direct observation of a new mechanism of deformation. This appears to consist, briefly, of dissociation of the grains into relatively coarse units, which can be observed and measured, and a process of flow by the bodily movement of these units within the parent grain. The mechanism predominates as the temperature becomes higher and the rate of deformation slower, and is probably that responsible for the quasi-viscous component of creep. It occurs without giving rise to the slip lines which characterize the more familiar deformation at normal temperature, and therefore gives the appearance of the "slip-less flow" noted by Hanson and Wheeler. Since the units are considerably coarser than the sub-microscopic crystallites involved in

deformation at normal temperature and rates of testing, they will be distinguished from the latter by the use of the term "cells".

II.—EXPERIMENTAL WORK.

After a preliminary description of the material used for the experiments (aluminium) and the relevant techniques, the observations are described most conveniently in the following order:

(1) Specimens deformed at various rates at room temperature. These will provide a standard of comparison.

(2) Specimens deformed at *slow* rates at elevated temperatures. These give the evidence for the cell formation.

(3) Specimens deformed at *faster* rates at elevated temperatures. These show how the cell structure is modified by the speed of deformation and therefore by the presence of the transient component of flow.

Finally, the results are discussed with reference to the two components of creep and to the strength of metals at high temperature.

III.—MATERIAL AND PRELIMINARY DATA.

The material employed was aluminium of 99.98% purity from which flat tensile specimens were obtained of $\frac{1}{8}$ in. thickness, $\frac{1}{2}$ in. width, and $1\frac{1}{2}$ in. length in the parallel test length.

The specimens were annealed to give a grain-size of approximately 0.2 mm. The X-ray back-reflection rings then consisted of sharp, separated reflection spots, a condition which has proved most suitable for observing the subsequent imperfections and breakdown of structure produced in the individual grains by plastic deformation. These stationary back-reflection photographs were obtained with $\text{CuK}\alpha$ radiation, which gave the (511), (333) rings. The transmission and Laue types of photograph, sometimes used for investigations of the present type, have been found much less sensitive and less informative.

When the specimens were in a suitable condition for the X-ray work, they were then polished so that they should be suitable also for metallographic examination under the microscope. The polishing was carried out electrolytically in order to obviate the surface deformation inherent in mechanical polishing. The electrolyte used was a standard perchloric acid-acetic anhydride mixture.

The extension of the specimens was carried out in various ways: by progressive loading with different time intervals between the loads; by allowing continued extension at a given load as in ordinary creep-testing; or, in special cases, by fixing one end of a specimen and attaching the other to a geared-down motor which forcibly extended the specimen at a constant strain rate of approximately 0.01%/hr. For the

experiments above room temperature, the specimens were held in a thermostatically controlled furnace.

IV.—SPECIMENS DEFORMED AT ROOM TEMPERATURE.

As already indicated, the X-ray and metallographic changes described in this Section are put forward to provide a standard of comparison. The specimens examined included

- (a) a specimen extended 10% in approximately 19 min.;
- (b) a specimen extended 10% in approximately 35 hr.;
- (c) specimens forcibly extended up to 10% at the constant rate of 0.01%/hr. The first two specimens were extended by tensile loading in increments of 160 lb./in.², applied in the first case at 30-sec. intervals to a final stress of 6180 lb./in.², and in the second case at hourly intervals to 5600 lb./in.²

It is necessary to consider one specimen only since the changes were essentially the same for each, being those characteristic of the normal mode of deformation by slip.

The changes shown by the X-rays for specimen (a) are illustrated in Figs. 1x and 3x (Plate XCIV), the former being taken before deformation and the latter after the 10% stretch. The feature to be noted for purposes of later comparisons is the transition from the sharp, discrete spots reflected from the initial perfect grains to the continuous and slightly diffuse rings typical of the deformed state. The occasional traces of reflection spots in Fig. 3x would disappear on further extension as the effects penetrated more uniformly throughout the grains. The interpretation of the X-ray changes has been discussed previously.⁵ It will be sufficient here to indicate that the *spread* of the initial spots to continuous arcs signifies a breakdown of the perfect grains into variously oriented elements reflecting over an appreciable angular range; and that the *continuity* of the arcs indicates a breakdown into a number of elements sufficiently large for the individual reflection spots from them to coalesce into an apparently continuous ring. It has been shown that this latter condition involves breakdown to a size less than 10^{-4} cm.; also that there is a limiting lower size to which the elements can be broken down by mechanical deformation at room temperature, a size which depends on the metal and for aluminium is about 5×10^{-5} cm. For this reason the elements have been termed "crystallites". The characteristic feature of deformation shown by the X-rays is therefore the reduction of the annealed grains to the crystallite formation.

The changes shown by the microscope are illustrated by Fig. 3m (Plate XCIV). (The magnification of this and all subsequent photomicrographs reproduced is 100 dia.) The condition before deform-

ation is not reproduced since it shows only the grain boundaries, as in a later illustration (Fig. 4*m*, Plate XCV). The feature to be noted here is the much studied change whereby the grains become traversed by systems of sharp slip lines, with their appearance of approximate parallelism and regular spacing. As is well known, they represent the dividing lines between parts of the grain which have slipped relatively to each other on deformation. Their relation to the crystallite formation shown by the X-rays is an interesting point, but is not pursued here, as it is desired only to discuss the modifications of each formation when the process of deformation is carried out at higher temperatures. The above-mentioned changes together will be regarded as characterizing the mechanism of deformation by slip.

V.—SPECIMENS DEFORMED SLOWLY AT ELEVATED TEMPERATURES.

The points brought out in this Section are that on slow deformation at a sufficiently elevated temperature the mechanism of deformation by slip is replaced by one in which the grains dissociate into a coarse cell-structure with absence of slip lines; that the process of deformation then involves the relative movement of these cells in the parent grains; and that these units or cells are not the product of recrystallization.

In order to limit the number of photographs for reproduction, the observations in the first place will refer to one typical specimen. This is a specimen at 300° C. allowed to extend under a single load of 530 lb./in.² and examined metallographically and by X-rays after various extensions. For each examination, the specimen was unloaded and cooled to room temperature. The regularity of the deformation-time curve was thereby disturbed, but it was not the object of these experiments to obtain quantitative curves or precise mechanical test data.

The specimen was examined after extensions of 1.2% reached in 2½ hr., 3.3% reached in 8½ hr., and 11.2% reached in 56 hr. The X-ray photographs obtained at these stages are reproduced in Figs. 4*x*, 5*x*, and 6*x*, respectively (Plates XCV and XCVI). The corresponding photomicrographs, showing the changes produced in the initially polished surface, are given in Figs. 4*m*, 5*m*, and 6*m* (Plates XCV and XCVI).

It will be seen that the changes shown by the X-rays are radically different from those observed with deformation at room temperature. The first feature is that the sharp reflection spots from the initial grains no longer degenerate into the continuous rings, but now break up into small groups of discrete reflection spots, each as sharp as the original. A second feature is that these secondary spots show a progressive scatter with increasing deformation; thus, after 1.2% extension the break-up of the initial spots is just discernible, after 3.3% it is easily

seen, while after 11.2% the scatter has so progressed that the general distribution is nearly uniform around the ring. The third feature is that the secondary reflection spots do not sub-divide in turn, because it was found that the number of reflections on the ring became approximately constant; thus, it was the same at 11.2% as after a further 10% extension. Finally, close examination will show that an initial spot divides into some 10-20 units.

These changes may be interpreted without ambiguity. The break-up of the initial reflections means that the original grains subdivide into discrete units, each perfect in structure; these have been referred to already as "cells". The progressive scatter of the secondary reflection spots means that the orientation of these cells departs slightly but progressively from that of the parent grain, and therefore that the slow deformation involves the relative movement of the cells within the grains. Further, from the number of reflections on the diffraction ring in the steady state, it is possible to deduce that the size of the cells must be about 10^{-3} cm., or approximately $\frac{1}{20}$ th of the initial grain-size.

The changes shown by the microscope are equally significant. It will be noted that in the photomicrographs reproduced here the same group of grains has been kept under examination, making it easier to follow the changes at each stage of deformation. As with the X-rays, the changes are quite different from those found at room temperature. The main difference is the non-appearance of the systems of slip lines. The surfaces of the grains become rumpled and exhibit faint striations, but these have no similarity to slip lines, as comparison with the earlier Fig. 3*m* will confirm. A second feature of the higher-temperature deformation is the progressive thickening of the grain boundaries, presumably the result of differences in level caused by relative bodily displacements of the grains. Finally, some evidence may be seen of migration of grain boundaries; but it should be added that this boundary mobility was not an important factor since in other specimens it was not observable. It may be concluded from these observations that the "slip-less flow," noted by Hanson and Wheeler is the mechanism whereby the grains deform by sub-division into the coarse cell formation.

Particular importance was attached to the further conclusion which could be drawn from the metallographic observations, namely that no recrystallization occurred during this deformation. The evidence was given conclusively by the observation that if at any stage in the deformation a specimen was repolished to remove all surface markings and then etched, the original grain boundaries would reappear. Therefore the cells are not grains finer than the original which have been formed by recrystallization; they are formed by direct sub-division of

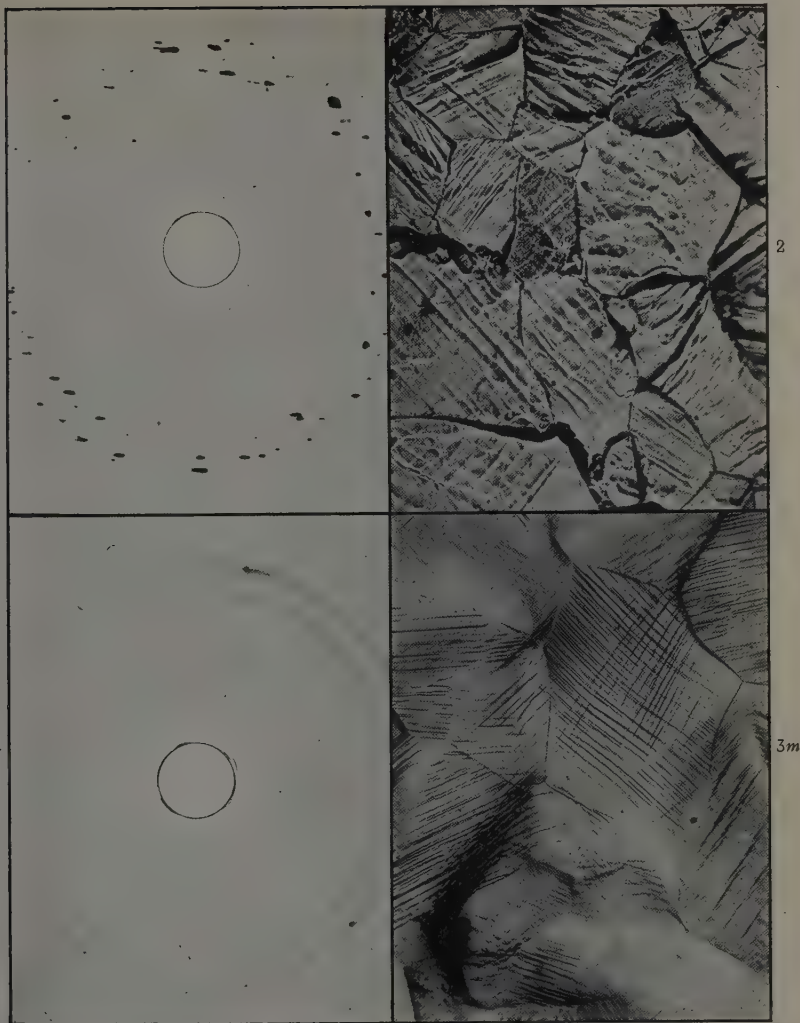
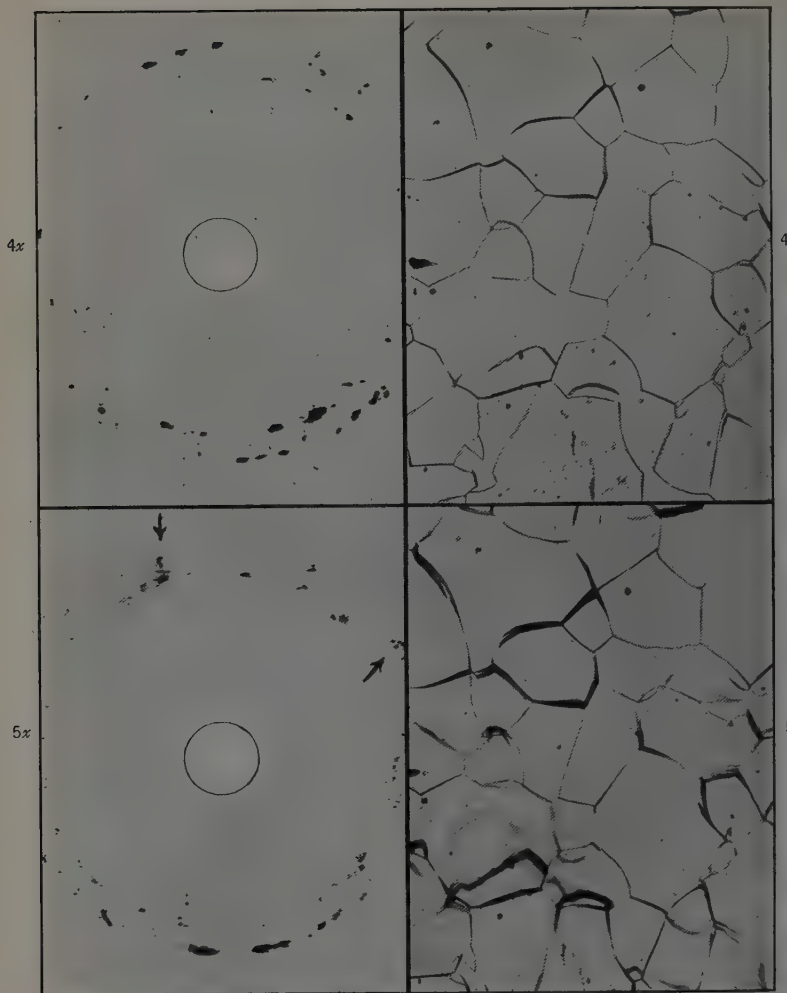


FIG. 1x.—Annealed State Before Straining.

FIG. 2.—Cellular Appearance in Grains After Slow 10% Extension at 250° C. Oblique illumination. $\times 100$.

FIGS. 3x, 3m.—X-Ray and Metallographic ($\times 100$) Changes After 10% Extension at Room Temperature.

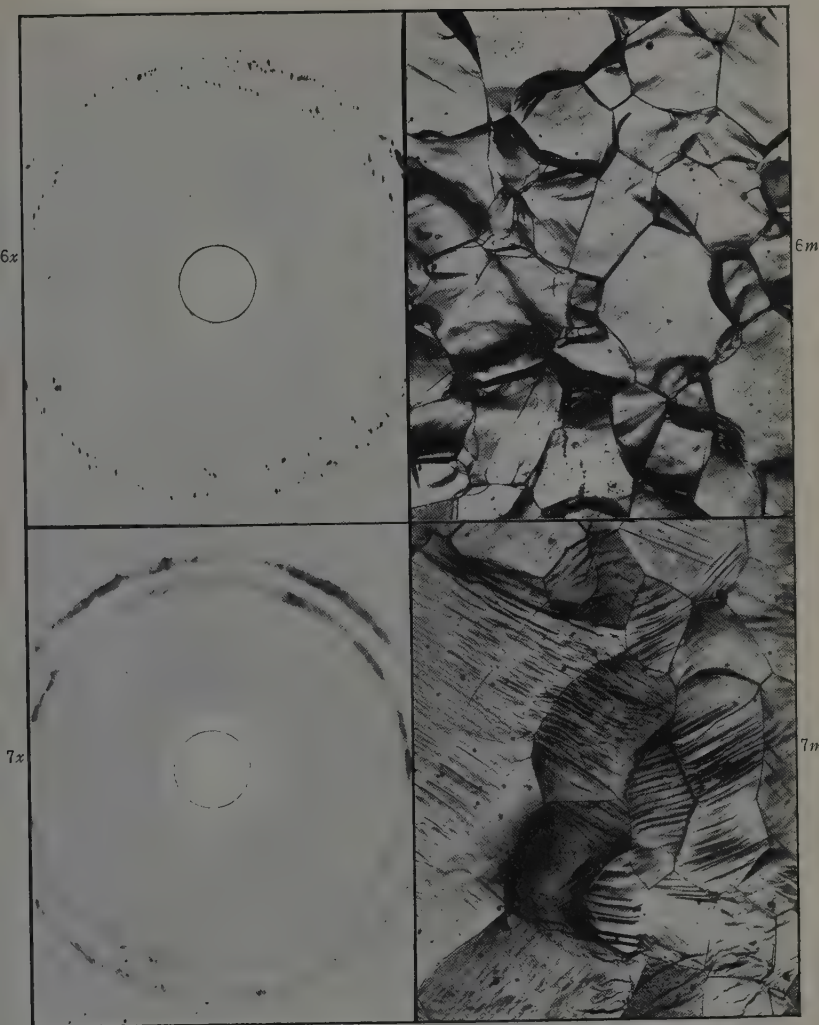
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FIGS. 4x, 4m.—X-Ray and Metallographic Changes After Creep at 300° C. (1.2% in 2½ hr., 530 lb./in.²).

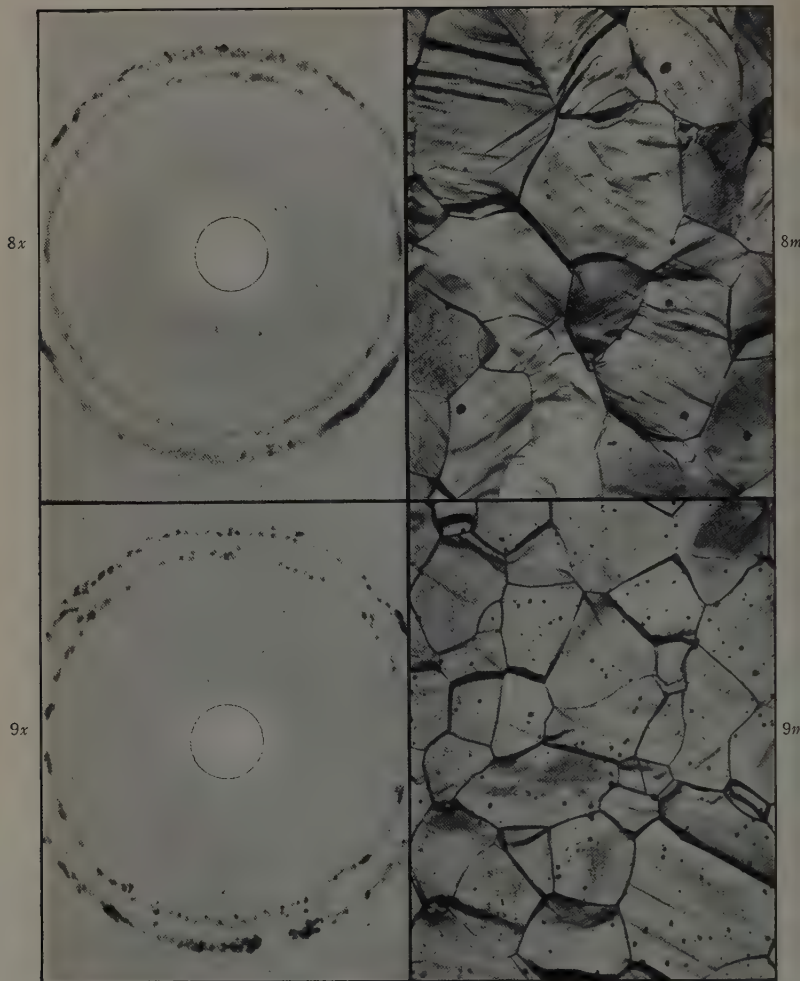
FIGS. 5x, 5m.—After Further Creep at 300° C. (3.3% in 8½ hr., 530 lb./in.²).

(Magnification of photomicrographs: × 100.)



FIGS. 6x, 6m.—After Still Further Creep at 300° C. (11.2% in 56 hr., 530 lb./in.²).
 FIGS. 7x, 7m.—Changes After Rapid Extension at 250° C. (9.6% in 7½ min., tensile loading).

(Magnification of photomicrographs: $\times 100$.)



FIGS. 8x, 8m.—Changes After Slower Extension at 250° C. (10% in 12 hr., slow tensile loading).
 FIGS. 9x, 9m.—Changes After Much Slower Extension at 250° C. (5% in 1060 hr., creep
 under single load of 550 lb./in.²).

(Magnification of photomicrographs : $\times 100$.)

the grains. This is in keeping with the X-ray photographs, which in the early stages of deformation definitely show a splitting-up of the original reflection spots, as described already (Figs. 4x and 5x).

The fact that the same grain boundaries persist, means also that the changes in orientation of the cells within the grains are not so large as to cause the grain entirely to lose its identity. This explains, moreover, why the cells have not previously been found by metallographic methods, for it is difficult by etching to bring up boundaries between grains or parts of grains showing only small differences in orientation. In view, however, of the very definite X-ray evidence for the presence of the cells, special attempts were made to see if they could be observed optically. The orientation between contiguous cells, according to the X-rays, need not differ by more than 1° , although from one extreme of a grain to another it could differ additively by the order of 10° . However, careful optical examination of specimens in which the X-rays indicated a cell structure always showed that the initially polished surfaces developed a network of cells on the surfaces of the grains after deformation. An example is shown in Fig. 2 (Plate XCIV); this corresponded to a specimen, specially studied, which was extended 10% at 250° C. in 12 hr. by loading in hourly increments of 160 lb./in.² In this specimen there were traces of widely spaced irregular slip lines, but in many of the grains the surface markings formed a cellular structure. The cellular appearance is clearly evident, specially if enhanced by oblique illumination as it was in this Figure. The interpretation of such surface markings is always difficult and the evidence is put forward tentatively. But it is significant that these markings were only observable in the specimens where the cellular structure was proved by the X-rays; also that they corresponded to cells always of the same order of size, and that this size was the same as that indicated by the X-ray photographs. Moreover it is reasonable to expect that since relative movements at grain boundaries produced marked differences in surface levels, thus emphasizing the grain boundaries (as is obvious from Fig. 2), similarly, relative movements at the boundaries of the cells within the grains should also alter the local surface levels and emphasize these sub-grain boundaries.

Thus the X-ray and optical observations may be summed up by saying that, at a sufficiently elevated temperature and a sufficiently slow rate of strain, the familiar mechanism of deformation by slip passes over to a mechanism based on the relative movement of a much coarser cell structure into which the grains sub-divide. The X-ray evidence is quite clear on this point. It remains next to consider how the transition is affected at different temperatures and different rates of strain.

VI.—DEFORMATION AT DIFFERENT RATES AT ONE TEMPERATURE.

In this Section it is shown that the effect of increasing the rate of strain at a given elevated temperature is to produce a mixture of the high-temperature cell formation and the room-temperature crystallite formation; also that the amount of the latter increases with rate of strain and is accompanied proportionately by the reappearance of slip lines.

(1) Consideration is directed first to the following specimens which were extended at the same temperature ($250^{\circ}\text{C}.$):

- (a) a specimen extended 9.6% in approximately $7\frac{1}{2}$ min.;
- (b) a specimen extended 10% in approximately 12 hr.;
- (c) a specimen extended 5% in 1060 hr. under a single initial load of 550 lb./in.²

The first two specimens were stretched by tensile loading in increments of 160 lb./in.², in the first case at 30-sec. intervals to a final stress of 2300 lb./in.², and in the second case at hourly intervals to a final stress of 1900 lb./in.²

The changes in the three specimens (a), (b), and (c) shown by the X-rays are reproduced respectively in Figs. 7*x*, 8*x*, and 9*x* (Plates XCVI and XCVII). The corresponding changes shown by the microscope are given by Figs. 7*m*, 8*m*, and 9*m* (Plates XCVI and XCVII).

The point at once evident from the X-ray photographs is that at the faster rates of strain the diffraction rings are composite. The numerous sharp spots indicative of the cell structure are superposed on the continuous ring characteristic of the crystallite formation. Therefore, both the mechanisms of deformation by slip and of deformation by the cell movement have been in operation. However, at the much slower rate corresponding to Fig. 9*x* the cell structure is predominant and a trace only of the continuous ring indicating the crystallite formation can be seen. Therefore at a sufficiently slow rate the cell mechanism only would be operative.

These points are confirmed by the corresponding photomicrographs. Thus systems of sharp slip lines are clearly evident in Fig. 7*m*, much less marked in Fig. 8*m*, and doubtful in Fig. 9*m*, which represents the condition of slip-less flow associated with the cell mechanism.

(2) Specimens extended at the somewhat higher temperature of $300^{\circ}\text{C}.$ are next considered. They showed, like the specimens described above, that at the faster strain rates both mechanisms were active, but at a sufficiently slow rate the cell mechanism of deformation only was operative. The effect of the higher temperature was that the latter mechanism predominated at higher strain rates than in the case of specimens tested at the lower temperature. In view of the general

similarity to the previous results, it is unnecessary to reproduce further photographs, but the observations are summarized in Table I. The observations under the heading "structure" indicate the points already mentioned, that the cell mechanism predominates at the lower rates of strain, and somewhat sooner than at 250° C.

It will be noted that the final hardness figures measured on the specimens are included. These are of interest in showing that the specimens are harder as the proportion of crystallite formation in the structure is greater; also that at the slowest strain rates the hardness of the specimens is little, if at all, greater than the initial hardness of the annealed material, which was 12-13 D.P.N. These hardness figures are interesting because it has been shown in other work⁶ that a metal becomes harder as the grains are fragmented by mechanical deformation

TABLE I.—*Structure and Hardness of Specimens Extended at 300° C.*

Specimen	Load, lb./in. ²	Duration	Extension, %	Structure	Hardness, D.P.N.
(a)	*	7 min.	10	Composite	17-19
(b)	*	9 hr.	10	Composite	...
(c)	520	97 hr.	6.6	Mainly cell	13.1-13.9
(d)	350	192 hr.	6.6	Cell	12.6-13.3
(e)	280	720 hr.	6.6	Cell	12.6-13.3

* Specimens (a) and (b) were extended by tensile loading in increments of 160 lb./in.² at intervals of 30 sec. and 1 hr., respectively. The remaining specimens were allowed to deform continuously under the single initial load indicated.

into elements of decreasing size. Therefore the specimens in which the structure is composite must in fact consist of a mixture of "hard" and "soft" regions; the former corresponding to grains or parts of grains where the small crystallite formation is most pronounced, and the latter to other parts where the coarse cell formation is predominant. Specimens consisting entirely of the cell formation, on the same view, must be very little harder than the original material, as indeed was observed; for such specimens could be regarded as annealed material with a somewhat finer grain-size than the original, except for the fact that the cells have much the same orientation in each parent grain.

(3) Further experiments were carried out at the still higher temperature of 350° C. The specimens included :

- (a) a specimen extended 9% in approx. 5 min. by tensile loading;
- (b) a specimen extended 10% in approx. 4 hr. by tensile loading;
- (c) a specimen extended at the constant rate of 0.01%/hr.

The first two were stretched, as before, by applying increments of 160 lb./in.² every 30 sec. and every hour, respectively. The third was extended in the machine for forcing a constant strain rate.

Specimens (a) and (b) showed the composite structure and specimen

(c) the cell formation alone. It was evident that the cell mechanism at this temperature tended to set in at faster strain rates than at the lower temperatures. Otherwise the results were similar to those at 300° C. and call for no further comment. Still higher temperatures were not used, in order to obviate the risk of introducing recrystallization.

In the above-described experiments on specimens deformed at different rates at a given temperature, it was necessary to decide if any vital significance could be attached to the point that the rapidly strained specimens were necessarily at the elevated temperature for a shorter time than those strained slowly. The possible effects of this factor could be studied by continuing to hold rapidly strained specimens at the same elevated temperature, in order to see if they developed a structure comparable with the slowly strained specimens. In no case did they do so. If the rapid straining had resulted in a composite structure with the crystallite formation greatly predominant, then the further heating produced recrystallization in occasional grains, but the recrystallized grains were much larger than the units of the cell structure. If the composite structure was one with the cell formation predominant, then the further heating caused no appreciable change in structure. Further heating of specimens in which the cell structure only was present caused no further change whatever. This means that, for the extensions and temperatures involved, the specimens in general were not deformed internally beyond the critical strain necessary for recrystallization and grain growth. No doubt, such conditions could have been induced by much heavier deformation, but they would have confused the issues.

Thus, the results in this Section may be summed up by the general observation that the effect of strain at the elevated temperatures was to produce a composite structure in which the cell formation was more pronounced the higher the temperature and the slower the rate of deformation. A further conclusion is that the cell formation could be produced only when the straining and heating were applied simultaneously. This point is of some importance in view of those theories which regard creep as the result of a running balance between strain-hardening and "recovery". All that is known about recovery has been obtained from experiments in which specimens have been strained at room temperature and then examined for changes in properties and structure resulting from subsequent heating. The structural changes thus produced are quite different from those found in creep. The former involve first a breakdown to the crystallite formation and then some degree of recrystallization. The latter is characterized by sub-division to a coarse cell structure direct, and retention of the original grains.

VII.—DISCUSSION.

Change in external shape of a specimen by mechanical deformation necessitates in practice a corresponding change in shape of the individual grains. This applies whatever the temperature or rate of strain.

In order to change shape a grain must divide into smaller elements so that one part may move relatively to the rest. At room temperature the elements are very small, and deformation results from relative translation of the elements between specific atomic planes, the so-called slip planes. At higher temperatures and slow rates of strain, the grains change shape by dissociation into much coarser elements, which, so far as can be judged, move relatively to each other without reference to specific slip planes. This appears to be the essential difference between the two modes of deformation.

Therefore, the new aspect to be considered in slow straining at elevated temperatures is the development in the grains of this coarse and irregular formation which, for the time being, has been described by the term "cell formation". However, before considering the actual process of deformation, it may be convenient to define more clearly the features of the formation as suggested by the X-ray and metallographic evidence already submitted.

Firstly, it would appear that the cell formation represents a definite sub-structure in the grains, analogous, in a way, to the sub-structure suggested by the slip lines in ordinary deformation at lower temperatures. This latter concept of a sub-structure tends perhaps to be hidden by the somewhat abstract theories of slip and dislocations which have been put forward by physicists in recent years, but it is quite fundamental to the slip process. It is more familiar to the metallurgist, having been brought out many years ago by the beautiful metallographic technique of earlier workers on plastic deformation, in particular by Rosenhain. This work showed that in deformation all atomic planes are not equivalent, but, in practice, only certain slip planes become operative; these lie roughly about 10^{-3} or 10^{-4} cm. apart, and break the contour of a polished surface by macroscopic steps also of the same order of size; thus it is a common experience that slip lines during deformation do not multiply indefinitely but tend to a statistical separation. This points clearly to potential planes of weakness and therefore to a virtual sub-structure of the grains essential for the change of shape required by deformation. In the same way, it is considered that the cell formation corresponds to an equivalent and equally essential sub-structure; but one which, presumably because of the greater atomic mobilities at the higher temperatures, is coarser in size and less closely bound up with specific atomic planes.

A second feature to be considered is the relative crystallographic orientation of the cells within the parent grain. It was found just possible with the normal metallographic procedure of polishing and etching to obtain evidence of the sub-boundaries within the grains, but only with difficulty. Therefore the neighbouring cells cannot differ greatly in orientation. On the other hand, the X-ray back-reflection technique, as already indicated, showed clearly a splitting of the reflections from the initial grains into secondary reflections during the slow deformation, and therefore proved definitely that some difference in orientation was developed. It is to be remembered that this technique is very sensitive; thus, in the conditions employed, a change in orientation of about 10° would move a reflection spot from one point on the reflection ring to a point diametrically opposite, or through 180° . The scatter of the secondary reflection spots, in the early stages of deformation when they could be followed, was over only a few degrees on the reflection ring. The corresponding scatter in the orientation of the cells within the grains would be only a small fraction of a degree. The metallographic and X-ray evidence together, therefore, show that the cells must have roughly similar orientations, but also that they must differ sufficiently in orientation to require boundary layers of atoms with transitional orientations. These layers will constitute sub-boundaries within the parent grain.

A third point to note is the progressive scatter in the orientation of the cells observed to occur during deformation. It is perhaps fortunate that such scatter does take place, for otherwise the discovery of the associated sub-structure would have been impossible even by the X-ray technique; also it would not have become evident that the change in shape of the grain involved the relative movement of the various parts of such a sub-structure. It is, however, a moot point whether the progressive scatter in orientations is an essential feature of the deformation process, and not a secondary effect arising from the inhomogeneous deformation inevitable in a polycrystalline aggregate. The important point is that the variations in internal orientation do make it possible to observe what is happening to the grain during the deformation.

The final point is that the parts of the sub-structure or cells appear to remain structurally perfect during deformation. This is shown by the observation that the secondary X-ray reflections from the cells are as sharp as the reflection spots from the initial annealed grains, and moreover remain sharp. This represents a difference from deformation by slip, which is supposed to result in lattice distortions and internal strains. If any such distortions occur during the high-temperature deformation by the cell mechanism they must be confined to the thin

transitional layers of atoms at the cell boundaries. This point is of importance, as discussed below, in relation to the degree of strain-hardening occurring during creep.

The above-mentioned points thus characterize the cell formation. In the more general case, of course, deformation will occur not only by the cell formation but also in some degree by the mechanism of slip and the finer crystallite formation. Both must be taken into consideration. It is suggested that the application to the problem of deformation at elevated temperature will then proceed along the following lines.

Firstly, it is to be noted that the breakdown of the grains to the small crystallite formation in the slip mechanism is accompanied by strain-hardening. This can be shown by experiment and also on theoretical grounds; it has been discussed fully in a recent paper by Wood and Rachinger.⁶ Thus, Sir Lawrence Bragg⁷ has shown that yield will tend to occur in a crystalline element when the elastic strain is of the order of d/l , where d is the atomic spacing and l the size of the element; therefore an element will stand a greater elastic strain before yielding as its size becomes smaller.

On the other hand, the dissociation of the grains to the much coarser cell formation will not be accompanied by appreciable strain-hardening because of the greater size of the cells. Some hardening may result because of the development of the associated sub-boundaries within the initial grains; but the hardening will not increase progressively with continued straining, firstly, because the cells do not become further reduced in size, and, secondly, and of equal importance, because their internal structure remains undistorted.

It follows that resistance to deformation at elevated temperatures, other things being equal, will be determined by the relative proportion and distribution of the two formations. If the cell formation predominates, then no appreciable strain-hardening will occur during deformation and the metal will flow continuously under stress as soon as any resistance inherent in the cell boundaries is overcome. Then we have quasi-viscous creep. So long as the cell formation is present in some degree in the metal there will be the possibility of continuous flow; but if the crystallite formation also is present and conditions of strain rate and temperature are favourable for production of the formation, each increase in deformation will tend to increase the crystallite formation at the expense of the cell formation; the crystallite formation will then tend to predominate and with it the associated strain-hardening until equilibrium with the applied stress is attained. Then we have transient creep. The rate of the quasi-viscous creep will depend on conditions at the cell boundaries and the effective internal

stress, which may differ from the external stress according to the distribution of any crystallite formation present, an essential feature of the present view being the observation that the metal during deformation is to be regarded as a mixture of "hard" and "soft" regions.

It is realized that a complete study of creep must include other factors. Thus, any structural fault which becomes unstable under increase of stress or temperature will contribute to deformation. Also emphasis has been given rather to the part played by the sub-structure of the grains than by the boundaries of the grains themselves. This, however, is regarded as correct, because the grains in practice cannot change shape by grain-boundary movements alone; but for the possibility of the internal deformation by relative movements of the sub-structure, the metal would quickly part at the grain boundaries and so fracture. There are also the factors of grain-size as well as possible tendencies to recrystallization to be considered.

But the problem of creep can be made so complex that it appeared necessary to reduce conditions in the first instance to the simplest terms. This procedure seems to have been justified because it has brought out what must be the major systematic mechanisms involved in deformation, and their relation to temperature and rate of strain. The associated structural changes will provide a future basis by which the effects of the many practical factors involved in creep can be logically assessed and compared. This view is confirmed by further work in progress in which other variables have been introduced. In order not to make the present paper unduly long it is proposed to treat these aspects separately, but it can be stated that they indicate already that the above-described concepts of the sub-structure in the grains, with its related properties, allow a number of previously empirical and apparently unrelated phenomena to be fitted together into a systematic picture.

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MODERN DESCRIPTIVE THEORIES OF PRECIPITATION PROCESSES.* 1177

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SYNOPSIS.

The object of the paper is to present a general picture of current theories relating to the precipitation process. The most recent theories describing precipitation in terms of a two-, three-, or four-stage process, involving the formation of Guinier-Preston zones, intermediate precipitate, and equilibrium precipitate, are briefly outlined. Their inter-relation and significance in regard to age-hardening is critically discussed and attention is drawn to aspects of precipitation phenomena for which no adequate explanation has yet been offered.

In discussing the relation between continuous and discontinuous precipitation, the suggestion is made that in any given system the latter will occur when the lattice strains are sufficiently great to cause fragmentation and recrystallization of the matrix. This point will be reached at different stages in different systems, thus accounting for the apparently haphazard occurrence of discontinuous precipitation.

It is known that partial reversion apparently inhibits subsequent re-aging. Split ageing treatments have been recommended for Al-Zn-Mg alloys, enabling maximum properties to be obtained with shorter ageing times. Short intervals of natural ageing, between quenching and artificial ageing, cause a reduction in the final properties of Al-Zn-Mg and Al-Mg-Si-Cu alloys. Possible explanations of these effects are suggested on the basis of the presence of particles of "precipitate" of different sizes and their influence on the subsequent ageing.

I.—INTRODUCTION.

THE problem of precipitation and age-hardening of supersaturated solid solutions may be approached from three angles. On the one hand there is the purely theoretical approach to the cause of the increased resistance to deformation, such as that of Mott and Nabarro.^{1, 2, 3} There is also the approach to the kinetics of the precipitation process, as in the work of Borelius^{4, 5} and Becker,^{6, 7} which aims at accounting for the rate of decomposition of the solid solution in terms of the free energy-composition and the rate of nucleation-temperature relationships. There are also the more descriptive accounts of the process of precipitation which have emerged from the studies of the resultant structural and physical changes.

It is too early to expect that the three approaches can be made to meet on any quantitative basis. Much more fundamental information

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is required before this can be anticipated. However, our knowledge of the process of precipitation is at a very interesting stage, and a complete description of the experimental findings is essential to the full development of the theoretical side. It is the purpose of this paper to review descriptions which have been given of the mechanism of precipitation, with particular reference to discrepancies, and to point out aspects of precipitation for which no adequate explanation has yet been offered. Full reviews of the structural and physical-property changes have appeared fairly recently,^{8, 9} to which reference should be made for an account of the more general phenomena.

The relationship between continuous and discontinuous precipitation is discussed first of all, as it is required for the account of the mechanism of the precipitation process. This is followed by a brief description of the effect of split-ageing and partial-reversion treatments.

II.—CONTINUOUS AND DISCONTINUOUS PRECIPITATION.

Mehl and Jetter⁸ describe four types of precipitation :

(a) *Ideal Precipitation* in which the distribution of precipitate is uniform and the concentration of the solute in the matrix decreases continuously and uniformly.

(b) *Continuous General Precipitation* in which the distribution of precipitate is uniform and the concentration of the solute in the matrix decreases continuously but not uniformly.

(c) *Continuous Localized Precipitation* in which the distribution of precipitate is non-uniform, with a preference for grain boundaries and slip planes. The concentration of the solute in the matrix decreases continuously in restricted regions, but with differences between these regions.

(d) *Discontinuous Precipitation* in which the distribution of the precipitate is non-uniform, spreading into the grains from the grain boundaries, and the concentration of the solute in the matrix decreases discontinuously. An example is given in Fig. 1 (Plate XCVIII). The areas, i.e. grain boundaries, in which precipitation starts promote the decomposition of the unchanged material, so that precipitation spreads towards the centres of the grains.

Real, as opposed to ideal, continuous precipitation may be regarded as a mixture of types (b) and (c). The further proviso may be added to discontinuous precipitation that it involves recrystallization and fragmentation of the matrix and may occur in single crystals. Broadly speaking, precipitation starts first at grain boundaries in both real

continuous and in discontinuous precipitation, but in the real continuous type this initial precipitation at the grain boundaries has no further influence on the course of precipitation as a whole, which becomes continuous throughout the crystals. On the other hand, in the discontinuous type the initial grain-boundary precipitation affects the whole course of the breakdown of the solid solution. The unchanged region immediately adjacent to this first-formed precipitate decomposes next and, since this is constantly occurring, the region containing precipitation spreads into the crystals from their grain boundaries (see Fig. 1). This propagation of a decomposed region into an unchanged region is an essential part of this definition of discontinuous precipitation.

Systems showing discontinuous precipitation usually show continuous precipitation as well, and it appears that discontinuous precipitation is often favoured by a high degree of supersaturation and a low ageing temperature.¹⁰ Nickel-beryllium alloys are apparently an exception to this, in that precipitation becomes more continuous with increasing supersaturation.¹¹ As far as is known (i.e. where it has so far been possible to check experimentally), discontinuous precipitation is always accompanied by the formation of the equilibrium precipitate.

In studying precipitation in aluminium-silver alloys, Geisler, Barrett, and Mehl¹² found that the change from the intermediate to the final precipitate * ($\gamma' \rightarrow \gamma$) was discontinuous. In Fig. 2 (Plate XCVIII) four crystals of the aluminium-silver alloy are shown, in which the intermediate precipitate has been formed having a uniform orientation within each crystal. These are the portions etched black in the photomicrograph. Growth of the equilibrium precipitate has started at the grain boundaries and is spreading into the crystals; these are the regions with a pearlitic structure. The bottom right-hand corner shows two colonies with different orientations within the same crystal. Since the equilibrium precipitate is also orientated with respect to the matrix, the colonies must be associated with recrystallization of the matrix.

Summarizing, the $\gamma' \rightarrow \gamma$ change is nucleated at the grain boundaries and involves recrystallization of the matrix, together with redistribution of the precipitate to fit the new orientation. This process is difficult to comprehend, as it must involve re-solution of the γ' phase, diffusion of the solute atoms, and precipitation on the orientation of the new crystals. However, the experimental findings are not in doubt. A suggestion

* The lattice of the intermediate precipitate is viewed as being continuous with the matrix while there is some form of interface between the matrix and the final precipitate (see Section III).

of major importance made by Geisler, Barrett, and Mehl was that the two-stage precipitation process (see Section III) :

Matrix \longrightarrow intermediate precipitate \longrightarrow equilibrium precipitate,
should more generally be written as :

Matrix \longrightarrow coherent intermediate lattice forming a Widmanstätten figure in matrix of unaltered orientation \longrightarrow non-coherent equilibrium precipitate plus recrystallized or re-orientated matrix.

On this view, discontinuous precipitation is not a primary type, but a structural change occurring late in systems that show normal continuous precipitation.

From a study of precipitation in a tri-crystal specimen of a copper-beryllium alloy, Guy, Barrett, and Mehl¹³ concluded that the discontinuous precipitation was due to an acceleration of the normal precipitation process by the stresses that are present at the boundary between two crystals of different orientations. It is also known that ordinary grain-boundary precipitation is greater, the greater the orientation difference between neighbouring grains.¹⁴

Gayler and Carrington¹⁵ have proposed an entirely different theory to account for the occurrence of both continuous and discontinuous precipitation in the same specimen. This requires that discontinuous precipitation occurs before continuous precipitation, which is apparently the case in silver-copper alloys. Discontinuous precipitation is favoured by a high degree of supersaturation, while continuous precipitation is favoured by low supersaturation. The occurrence of continuous precipitation is accounted for by assuming that it takes place when the solid solution has become depleted in solute by the discontinuous precipitation. But the objection to this is that the whole of the crystal would have to provide solute for discontinuous precipitation, and this mechanism requires diffusion over improbably long distances. Also, it is not clear how this could happen without altering the lattice spacing of the unchanged solid solution, as actually both the original and final solutions co-exist.

The present author suggests that a generalized theory can be put forward to account for the occurrence of discontinuous precipitation at various stages in the different systems. This is that the fragmentation and recrystallization, which initiate discontinuous precipitation, will occur at the particular stage in the process of precipitation at which the lattice strain set up is sufficiently great to provide the necessary energy. Owing to the misfit between neighbouring crystals, there will be a high

degree of lattice strain at the grain boundaries of the quenched solid solution. Nucleation of precipitate occurs most readily in such regions, thus rapidly increasing their lattice strain. If this immediately reaches a sufficiently high value, fragmentation (and recrystallization) will proceed and give the typical form of discontinuous precipitation spreading into the grains before continuous precipitation has started. On the other hand, if the build-up of lattice strain at the grain boundaries occurs more slowly, continuous precipitation will have started before the discontinuous type commences. This does not rule out discontinuous precipitation in single crystals, although in this case it will originate from lattice defects other than grain boundaries. Two systems showing the extreme types of behaviour will be mentioned.

It may well be that in some systems, such as copper-beryllium, the supersaturated solid solution is so heavily strained that recrystallization and the initial precipitation proceed almost simultaneously at the grain boundaries. On the other hand, in the aluminium-silver system the lattice strain for recrystallization does not become sufficiently great until an easily recognizable intermediate precipitate is present. Other systems will fall between these two extremes, thus accounting for the apparently haphazard occurrence of discontinuous precipitation. On this basis, anything increasing the lattice strain should increase the tendency towards discontinuous precipitation. This may well account for an added preference towards this form at low temperatures and high degrees of supersaturation.

The apparently anomalous behaviour of the nickel-beryllium system, in which continuous precipitation is favoured by high supersaturation, requires further investigation. It is a pity that nothing is known of the mode of precipitation of gold-platinum and platinum-gold alloys, in which the variation of the rate of precipitation with supersaturation has been extensively studied.¹⁶ In this system, slow precipitation at low supersaturation (and high temperatures) was ascribed to the alloys being in a region of the equilibrium diagram in which the term $\partial^2 F / \partial C^2$ becomes positive (F = free energy, C = concentration). Borelius⁴ suggests that this would directly decrease the probability of nucleation, although other views are possible to account for the slowness of precipitation under such conditions.^{6, 7} If this system should be found to show discontinuous precipitation, metallographic and X-ray evidence, in combination with the known rates of precipitation, would prove of great interest in the study of the relation between continuous and discontinuous precipitation and of precipitation theory generally.

III.—DESCRIPTIONS OF THE PRECIPITATION PROCESS.

Since Wilm's original discovery, major interest in age-hardening has always been centred on the aluminium-copper alloys. These show nearly all the complexities found in other systems, and in many ways are unique in the clarity with which various effects can be distinguished. Although other systems have also been studied intensively, it is proposed to concentrate on the aluminium-copper alloys, drawing on information from other systems mostly for comparison purposes.

The sole requirement for producing precipitation phenomena is a change of solubility with temperature, together with the ability to produce a metastable supersaturated solution by rapid cooling. At the moment the mechanism of precipitation is described in terms of a two-, three-, or four-stage process, which may or may not involve the fragmentation and recrystallization of the matrix. All workers are agreed that on ageing aluminium-copper and aluminium-silver alloys at fairly low temperatures the equilibrium precipitate does not occur until a relatively late stage in the process, and that it is formed from a precipitate with an intermediate structure. In the aluminium-copper system the equilibrium precipitate is designated θ (or CuAl_2 or $\beta\text{-CuAl}_2$): the transitional intermediate structure of the precipitate is denoted as θ' (or $\alpha\text{-CuAl}_2$). In the aluminium-silver system the stable precipitate is γ and the intermediate precipitate γ' . The lattice relationships between the solid solution and the various precipitates of the aluminium-copper alloys are shown in Fig. 3 (Plate XCIX).

There is disagreement between the various investigators as to how the lattice of the intermediate precipitate is formed from the supersaturated solution, but after this stage has been reached there is general agreement on the existence of θ and θ' , and there are no real discrepancies in the orientation relationships assigned to the lattices of the various phases. It is also agreed that the lattice of the intermediate phase is continuous with the matrix. The intermediate precipitate is so orientated that its atomic pattern on the matching plane is almost identical with that of the matrix. Continuity of the lattice remains as long as the mutual lattice strain* in the matrix and the precipitate, due to any slight disregistry in their atomic spacings, can be withstood. When these strains become too great, owing to growth of the intermediate precipitate, this breaks away and transforms into the equilibrium structure with the formation of a boundary surface with the matrix.

The nature of the boundary interface between the equilibrium matrix

* This is called "reciprocal lattice strain" by Barrett and his co-workers. The term has been avoided here because of the possibility of confusion with the "reciprocal lattice" used in crystallography.

and the equilibrium precipitate is a matter for speculation at the moment. The difference in lattice parameter means that there will be islands in the interface where the atomic misfit between the two lattices is complete, and these will be surrounded (or *vice versa*) by regions in which the atomic fit is fairly good. In the latter regions there will certainly be interaction between the atoms in the two lattices, but this will be of an entirely different degree from that in regions where the degree of misfit is high. Thus, the equilibrium precipitate differs from the intermediate precipitate, as in the latter the atomic fit is good over the whole matching plane and is retained in this condition by a certain degree of lattice strain. It is the high degree of atomic misfit which brings about the relative discontinuity at the interface between matrix and equilibrium precipitate.

It is further agreed that it is this mutual lattice strain between the matrix and the "precipitate" in its early stages of formation which is responsible for the increase in hardness on ageing. Maximum strength is obtained when the number and size of the particles cause the maximum effective lattice strain.

The various steps which have been assigned to the formation of the intermediate precipitate are discussed below.

1. *Precipitation as a Two-Stage Process.*

Matrix \longrightarrow *intermediate coherent precipitate* \longrightarrow *equilibrium precipitate.*

Barrett and his co-workers^{17, 12} (aluminium-silver alloys), together with Fink and Smith¹⁸ (aluminium-copper alloys), believe that the intermediate phase is formed immediately the supersaturated solid solution starts to decompose, and exists in a strained state coherent with the parent lattice. Evidence of the structural state, prior to an easily recognizable transitional precipitate, is based on the interpretation of streaks on the Laue X-ray diagram. As discussed by Barrett and Geisler¹⁹ there are two possible causes of these streaks: firstly, the occurrence of small plate-like clusters of solute atoms parallel to certain planes in the matrix (this is the original theory of Guinier and his colleagues^{20, 21} and Preston^{22, 23}); or, secondly, the formation, parallel to the same planes in the matrix, of extremely thin lamellæ of the transitional precipitate. The former could cause streaks by a difference in scattering power of the solute and solvent atoms. The latter structure could act as two-dimensional gratings and thus give rise to streaks, since it lacks periodicity in one direction. Barrett and his co-workers favour the second explanation, chiefly because the same phenomenon of streaks was found in the Laue patterns of aluminium-magnesium alloys.²⁴ In their view this rules out the first explanation, as the aluminium and

magnesium atoms both have similar scattering power, and in this case the streaks would only arise from a change in lattice dimensions.

There is, however, a point in the work on aluminium-magnesium alloys²⁴ which militates against the general applicability of the interpretation of Barrett and his colleagues. Apparently the first change towards streaks in the Laue diagram is not observed until considerable hardening has occurred, when some form of microscopic change is also well established. This implies that in this system the streaks are most probably due to a slight shift in lattice dimensions, but since segregation had obviously occurred, or platelets had been formed before being detected as streaks, the possibility that the streaks on the Laue diagrams of other systems are directly attributable to segregations is not ruled out.

Geisler²⁵ has recently discussed the property changes on ageing exclusively from the point of view of the two-stage mechanism. He believes that all the evidence can be accounted for on the basis of a coherent intermediate precipitate without recourse to any further steps.

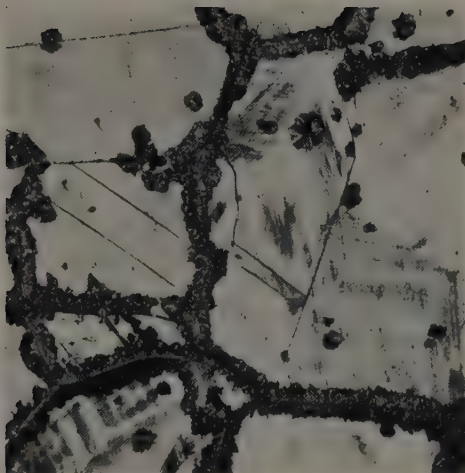
In a very recent paper Geisler and Hill²⁶ have re-examined the causes of streaks on the Laue diagrams of aged alloys. These are interpreted as being due to a coherent precipitate differing in structure from the matrix. The changes in the X-ray pattern are ascribed entirely to the effect of variation in size of the particles of the coherent intermediate precipitate.

The first change in a quenched alloy (Al-Mg₂Si) is to form "string-lets" of the new structure which may possess a preferred crystallographic direction; "platelets" form later. When the X-ray pattern of these was transferred to the crystallographic reciprocal lattice they took the form of rods corresponding to the plate-like structure in the matrix. The fact that these rods did not necessarily pass through the points of the reciprocal lattice representing the matrix planes was taken as evidence of a new structure rather than of simple segregation. Also these rods in the reciprocal lattice corresponded more closely to the points representing the planes of the intermediate precipitate. In aluminium-copper alloys Preston²² found that the rods corresponding to the platelets did pass through the matrix spots in the reciprocal lattice, but extended unequally on either side of them, so that for these alloys evidence for segregation is stronger.

2. Precipitation as a Three-Stage Process.

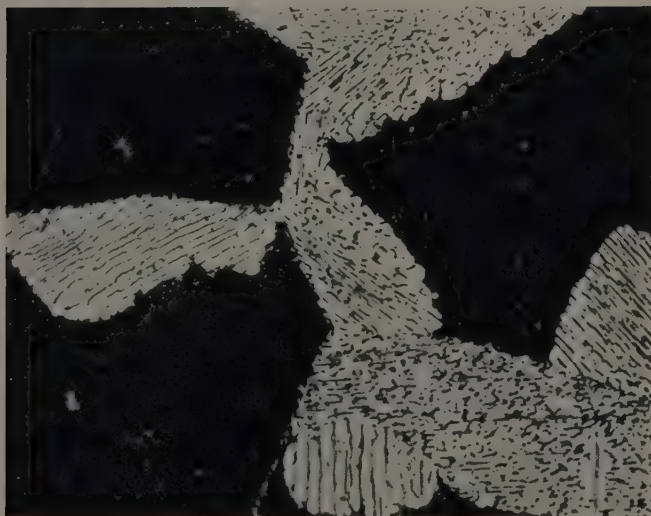
Matrix \longrightarrow *Guinier-Preston zone* \longrightarrow *intermediate coherent precipitate*
 \longrightarrow *equilibrium precipitate.*

Gayler and Parkhouse,²⁷ Preston,^{22, 23} and Guinier and his co-workers^{20, 21} have favoured the existence of a three-stage process involving,



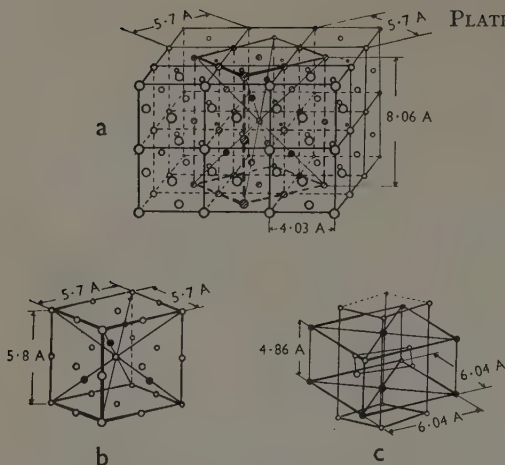
[Courtesy American Society for Metals.]

FIG. 1.—Typical Discontinuous Precipitation Starting from Grain Boundaries in a Cu-Be-Fe Alloy Aged for 2 hr. at 325° C.⁸ × 70.



[Courtesy American Institute of Mining and Metallurgical Engineers.]

FIG. 2.—Microstructure of Aluminium-20% Silver Alloy Aged 6 hr. at 303° C., Showing the Formation of Nodules with a New Orientation Containing Plates of the Equilibrium Precipitate γ . This involves a discontinuous change from the matrix, etched black, which contains the intermediate precipitate γ' .¹² × 1000.



[Courtesy American Society for Metals.]

FIG. 3.—Lattices in Precipitation in Aluminium-Copper Alloy. Full circles are copper atoms, hollow circles are aluminium atoms. The lattices are drawn to show the orientation relationships :

- (a) Aluminium-copper solid solution before precipitation. The inscribed tetragonal prism shows the grouping of atoms which becomes θ' unit cell in (b). The four copper atoms in the centre of the tetragonal prism are retained in the θ' lattice: the aluminium atoms occupying the corresponding positions are lost.
- (b) The θ' lattice.
- (c) The θ , CuAl_2 lattice, not the unit cell, drawn to show orientation relationships and to include a grouping of atoms comparable to that of (b). Successive horizontal layers are equidistant at 2.43 kX. units.⁸

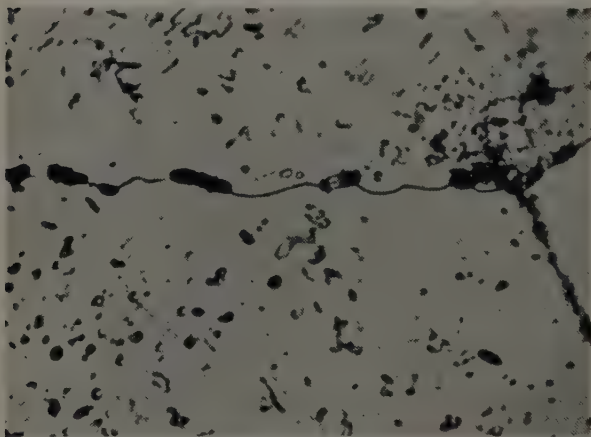


FIG. 4.—Aluminium-4% Copper Alloy Aged 80 days at 130° C. Etched 1 min. in 25% HNO_3 at 70° C., and then swabbed with $\frac{1}{2}$ % HF. Shows pits at the horizontal grain boundary connected by patches of the "light phenomenon" (or crystallites).²⁹ Original $\times 2000$; reproduction $\times 2300$.

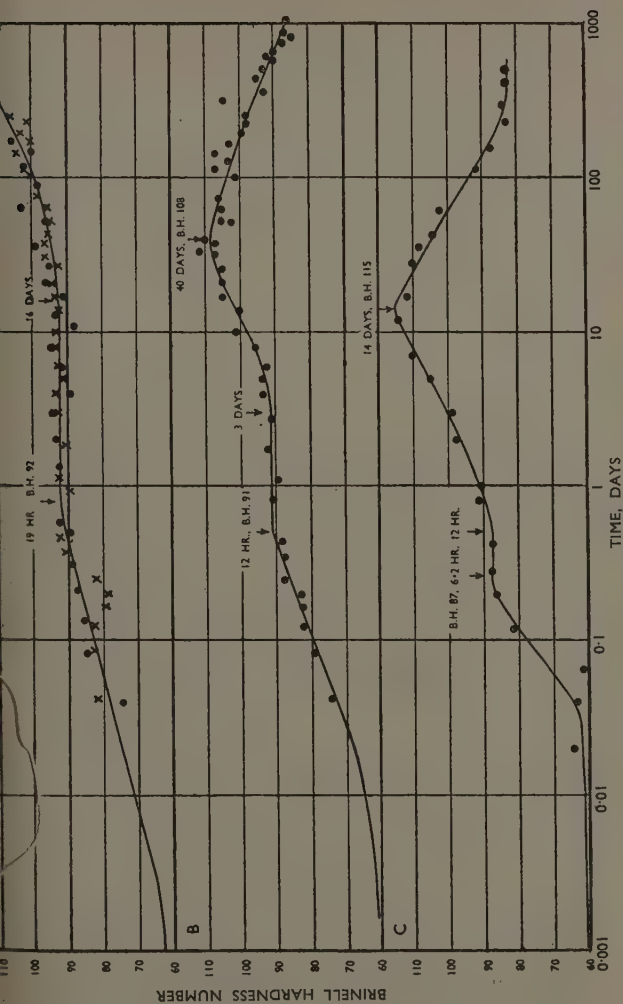


Fig. 5.—Time-Hardness Curves of an Aluminium-4% Copper Alloy (Gayler and Parkhouse 27).

A. Ageing temperature 100° C.

x = Specimen quenched from 500° C.; as quenched, Brinell hardness = 63. Mean of two impressions.

• = Specimen quenched from 520° C.; as quenched, Brinell hardness = 62. Mean of three impressions.

B. Ageing temperature 130° C.; quenching temperature 500° C.; as quenched, Brinell hardness = 60. Mean of two impressions.

C. Ageing temperature 148° C.; quenching temperature 535° C.; as quenched, Brinell hardness = 58. Mean of three impressions.

as an additional step before the formation of an intermediate precipitate, the segregation of solute atoms on certain planes of the matrix. These plate-like segregates are variously known as Guinier-Preston zones, "knots", or θ'' , but will be referred to here as G.P. zones.

Gayler and Parkhouse recorded the occurrence of two stages in the increase of hardness with time of ageing of aluminium-4% copper alloy at elevated temperature²⁷ (Fig. 5). The original theory associated the first increase in hardness with the G.P. zones. The flat portion and the second increase (see Fig. 5) were associated with the formation of the coherent intermediate lattice due to the lattice strains set up between the matrix and the precipitate; while the subsequent softening was explained by the formation of the non-coherent equilibrium precipitate which was recognizable in the microstructure at this stage.

3. *Precipitation as a Four-Stage Process.*

Type (a): Matrix \longrightarrow G.P. zone [1] \longrightarrow G.P. zone [2] \longrightarrow intermediate coherent precipitate \longrightarrow equilibrium precipitate.

Guinier has deduced a four-stage process from further X-ray work,²⁸ there being two steps in the formation of knots. The first stage involves the segregation of copper atoms in localized regions on (100) planes, with an irregular distribution in the matrix lattice; the second stage is a further segregation of copper atoms on certain favoured (100) planes having a periodic distribution within the localized regions. By some means yet unexplained, the excess aluminium atoms (Fig. 3, Plate XCIX) are expelled, and when the copper and aluminium are in the right proportions, there is a lattice contraction of the G.P. zones perpendicular to the (100) planes of the matrix from 8.06 to 5.80 crystal Angstroms, with the formation of θ' . This transformation takes place suddenly. At a later stage this intermediate precipitate changes into the equilibrium precipitate.

Type (b): Matrix \longrightarrow G.P. zone \longrightarrow precipitation of copper-rich aggregates with relief of lattice strain, their growth and formation of new aggregates \longrightarrow intermediate coherent precipitate \longrightarrow equilibrium precipitate.

In a recent paper on the aluminium-4% copper alloy, Gayler²⁹ discusses the two stages in the hardness curves (Fig. 5), in the light of a further metallographic examination.

The following microscopic observations were recorded as the specimens approached maximum hardness (at 130° C.).²⁹ While on the flat portion of the hardness-time curve the specimens have increased chemical reactivity, shown by etching pits in the grains and grain boundaries when etched with hot nitric acid. The shape of the pits is ill-defined,

but, arguing from their general similarity, their cause is ascribed to changes, on a sub-microscopic scale, similar to those which can be seen on a microscopic scale as the rise to maximum hardness proceeds. Close to maximum hardness, larger etching pits are developed and, if the specimen is further etched with an etching reagent containing hydrofluoric acid, white regions (crystallites) are visible immediately adjacent to the pits (see Fig. 4, Plate XCIX). This effect is clearly seen at the grain boundaries, but, although easily detected visually, cannot actually be distinguished inside the crystals in the photomicrographs.²⁹ No particles of θ' were detected till well past the maximum hardness. That the etching pits were not finely divided θ' was shown by their reaction to dry hydrogen sulphide vapour. θ' was unattacked, but regions similar to those which would give etching pits with nitric acid were stained black. The deduction drawn from this was that the etching pits corresponded to regions rich in copper.

It is believed that the following summary represents Gayler's theory on the cause of the flat portion and the second increase on the hardness curve, based on the above microscopic observations.²⁹

During the first stage of ageing segregation of copper atoms takes place on (100) planes of the matrix (G.P. zones). This process is brought about by diffusion and causes strain-hardening, leading to the first increase in hardness. As the number of aggregates grows, so does the strain-hardening, until no more diffusion of copper atoms can occur and no further increase in hardness is observed.

The flat portion of the hardness-time curve is the result of two processes. Relief of strain occurs by precipitation of sub-microscopic copper-rich aggregates of a critical size, with the formation of their associated sub-microscopic crystallites of the aluminium solid solution of equilibrium concentration. This would cause softening, but is balanced by diffusion of copper atoms leading to the formation of copper-rich aggregates in regions which are freed from lattice strain by this precipitation. Further hardening eventually results, as localized diffusion of copper atoms increases the size of the aggregate to a visible size.

Gayler further suggests that precipitation in the aluminium-4% copper alloy should be regarded as discontinuous, since the copper-rich aggregates are associated with crystallites of the solid solution probably of equilibrium composition.

The flat portion of the hardness-time curve corresponds to the ageing conditions at which Guinier³⁰ observes the clusters of copper atoms forming on (100) planes with a periodic distribution. Taking this as the structure corresponding to the etching pits, mechanisms of type (a) and (b) are essentially the same, except that the latter includes the

simultaneous formation of crystallites. Mechanism (b) allows a theory to be developed to account for the stages in the hardening curve, when used with the hypothesis that crystallite formation is associated with relief of strain.

4. *Precipitation as a Five-Stage Process.*

Matrix \longrightarrow "stringlets" \longrightarrow G.P. zone [1] \longrightarrow G.P. zone [2] \longrightarrow intermediate coherent precipitate \longrightarrow equilibrium precipitate.

If Geisler and Hill's ²⁶ recent observation of "stringlets" preceding the formation of "platelets" is found to have general existence, and if it is also found to be due to segregation of solute atoms, then the mechanism of ageing may involve the five-stage process postulated above.

5. *Discussion of Descriptive Theories.*

The discrepancies between the interpretations of the Laue streaks, advanced by Guinier and Preston, on the one hand, and by Barrett and his colleagues on the other, are not easily resolved. Indeed, Guinier goes so far as to suggest that γ' , the intermediate lattice in the aluminium-silver precipitation, has no separate existence, the change being directly from the G.P. zone to the equilibrium precipitate γ .

Barrett interprets the streaks found in aluminium-magnesium alloys as proof of a difference between the lattice spacing of the matrix and the solute-rich portion. Guinier and Preston associate the streaks with clusters of solute atoms, as a result of the difference in scattering powers of the solvent and solute atoms. Both views are equally acceptable theoretically. It has already been pointed out that the evidence from the aluminium-magnesium system ²⁴ (see Section III. 1.) is not conclusive proof of a difference in spacing for all cases where streaks are found on the Laue photograph. In aluminium-copper alloys streaks occur when the platelets are sub-microscopic; in aluminium-magnesium alloys the platelets are evident microscopically before the streaks.

Geisler and Hill's paper ²⁶ shows that the first step in the ageing mechanism is the formation of "stringlets". Their finding, that the rods in the crystallographic reciprocal lattice, corresponding to the streaks on the X-ray pattern, do not necessarily pass through the matrix spots, is certainly strong evidence that there is some factor playing a part in the process as well as simple segregation. It is still not clear, however, that this can be regarded indisputably as the formation of a new structure. These authors point out that streaks are found in aluminium-silver alloys in which the solid solution shows no lattice-parameter change with composition. They take this as evidence in favour of their

theory that the streaks are due to the intermediate coherent precipitate, although the effects could also be caused by segregation of atoms of dissimilar scattering powers.

Both Guinier and Preston state, more or less incidentally, that there will be a slight change in lattice parameter with such an aggregation of solute atoms. The lattice shift they visualize would inevitably be less than that postulated by Barrett, but there seems no reason why both causes should not be capable of reinforcing one another. Their relative importance would depend on the scattering powers of the two kinds of atoms, together with the lattice shift associated with a cluster of a particular type of solute atom, and further theoretical work is required along these lines.

The three-stage process of precipitation as the explanation of the hardness-time curve of aluminium-copper alloys must be ruled out in view of Gayler's later metallographic results, which show that the rise to the second maximum is still associated with a structure possessing etching characteristics different from θ' . This latter is recognizable only later in the precipitation process. From this work it is clear that an aggregation of copper atoms prior to the formation of θ' is a real structure and an essential part of the precipitation process.

It is obvious that many of the views outlined above are extremely conflicting. In the writer's opinion they can be best drawn together in the following manner. The essential point is whether segregation leading to G.P. zones precedes the formation of an intermediate coherent precipitate. It is believed that streaks can arise from plates of segregation accompanied by slight change in lattice dimensions, as well as from larger changes in lattice dimensions equivalent to the formation of a new structure. To a considerable extent this difference will be one of degree only. The exact stage at which ageing leads to the formation of an intermediate coherent precipitate will depend very greatly on the ability of the solvent and solute atoms to occupy "wrong" positions in its lattice, i.e. to interchange lattice sites. Where this ability is limited and the structure of the intermediate coherent precipitate demands a high degree of order, there will be a stronger tendency to form and retain G.P. zones. This appears to be the case in aluminium-copper alloys. The actual lattice spacing may well vary over the platelet, depending on the extent to which the sorting out of the atoms into their correct positions has occurred. In other systems this tendency may well be much weaker, and these will be more likely to form a separate structure at an earlier stage. This may account for Geisler and Hill's observations²⁶ on the position of the rods in the reciprocal lattice corresponding to the streaks in the Laue diagram.

The chief criticism of Gayler's theory lies in the explanation of the flat portion of the hardness-time curve. The way in which copper-rich aggregates can "precipitate" to allow relief of strain without forming a new phase is by no means obvious, since this "precipitation" would imply a loss of coherency with its consequent opportunity for atomic rearrangement. The occurrence of the crystallites associated with the etching pits was described as evidence of discontinuous precipitation. But if we accept the Mehl and Jetter definition⁸ of discontinuous precipitation, an essential part of which involves the activation of the unchanged matrix along its boundary with regions containing precipitation, the phenomena can probably be explained on the basis of real, rather than ideal, continuous precipitation; that is, types (b) and (c) of Section II. Real precipitation implies a slightly non-uniform variation in solute concentration of the matrix. The precipitation is affected by grain boundaries and lattice irregularities, in whose immediate neighbourhood a more rapid depletion of the solid solution is to be expected compared with the remainder.

If the relief of lattice strain were necessary at this stage, "precipitation" of copper-rich aggregates would only allow such relief if there was a loss of coherency between the cluster and the matrix lattice. The following alternative explanation is offered of the two-stage hardening in aluminium-copper alloys, based on the view that in this system the G.P. zones have a real existence separate from θ' .

The first increase in hardness is associated with the formation of G.P. zones [1], small in size, large in number, and of random distribution. The increased resistance to deformation on ageing is accounted for by the mutual lattice strain between the matrix and the "precipitate". As pointed out earlier, maximum strength is obtained when the number and size of the particles of "precipitate" cause the maximum effective lattice strain. This is a function of the size of particles, the lattice strain per particle, the number of particles, and the lattice strain due to solute atoms still unagglomerated within the solid solution.

Equilibrium and metastable equilibrium between a precipitate and a solution must be regarded as a dynamic rather than a static affair, in which solute atoms in the precipitate will change place with solute atoms in the matrix. On this basis, the flat portion of the hardness-time curve is to be regarded as a period during which the smaller G.P. zones [1] re-dissolve slowly, the solute atoms joining the larger G.P. zones [1]. These form the G.P. zones [2] with a periodic distribution, the whole of this action occurring within very small regions of the matrix. It is probable that the G.P. zones [2] possess a relatively much larger volume of material subject to lattice strain immediately around them than the

G.P. zones [1], the conditions being such that the hardness is again increased. The actual position of a hardness maximum due to the lattice strain is a very complicated balance of hardening, this being greater the larger the agglomeration of solute atoms, and softening taking place by a reduction in the number of such agglomerations and by the rejection of solute atoms from the rest of the matrix.

Softening after the maximum hardness is then associated with the further growth of the coherent G.P. zones [2] past the critical size for maximum effective lattice strain, together with the formation of the θ' lattice.

Two possible mechanisms exist for the mode of formation of θ' from the G.P. zones. Transformation of solid solution to θ' requires no change in atomic spacing in the (100) plane of the matrix, while there is a contraction perpendicular to this plane from 8.06 to 5.70 crystal Angstroms. It is not known how the excess aluminium atoms (Fig. 3, Plate XCIX) are actually ejected and the formation of θ' , which is reported to occur as a rapid jump, may represent the stage at which these have finally been expelled. On the other hand, it is possible that the change to θ' represents the formation of one interface with the matrix, say, around the outside cylindrical surface of the platelets (which is the form taken by the G.P. zones). On this view the aluminium atoms would have been lost at some earlier stage by simple diffusion, the G.P. zone [2] then being analogous to a "defect" lattice. This suggestion is in good agreement with the sudden formation of θ' , which would occur when the mutual lattice strains had exceeded a critical value, and could probably be tested by X-ray single-crystal analysis.

Transformation of θ' to θ is a more complicated atomic re-arrangement and, irrespective of the mechanism of formation, will require the complete loss of coherency with the matrix lattice. This occurs when the coherency strains can no longer be withstood. That it is a polymorphic transformation occurring gradually within the particles of θ' is suggested by Gayler's work.³¹

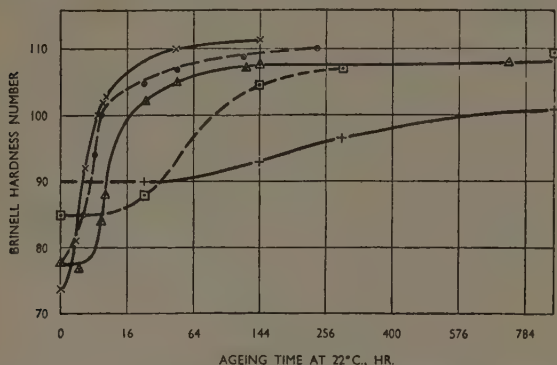
IV.—REVERSION AND SPLIT AGEING.

Although present theories of the precipitation process have not been materially assisted by studies of reversion, an account is given of the present position in this field, since it is believed that more use could be made of such work in relation to sizes of "precipitates".

Reversion is the loss of hardness or other properties produced by a very short heating above the ageing temperature and subsequent re-ageing at the lower temperature. It has been fairly extensively studied

on aluminium-copper³² and Duralumin-type alloys,³³ the effects occurring only to a much lesser extent in other systems.³⁴

It is now generally accepted that the softening is due to the dispersion of the nuclei (G.P. zones) formed at the lower temperature, when these are below the critical size for growth at the higher temperature. Thus, on very short heating at an elevated temperature (220° C. for naturally aged aluminium-copper alloys) the heterogeneity due to the segregates is



[Courtesy "Zeitschrift für Metallkunde".]

FIG. 6.—The Room-Temperature Re-Ageing of a Duralumin-Type Alloy After Short-Time Heating at Elevated Temperatures (Dreyer³³). A hardness below 80 may be taken as signifying almost complete reversion; a hardness above 80 implies partial reversion only.

KEY.

× — ×	Quenched from 500° C.
○ --- ○	Aged for 2 min. at 240° C.
△ — △	" 5 " 220° C.
□ --- □	" 5 " 200° C.
+ --- +	" 5 " 180° C.

lost and the alloy will re-harden when brought back to the lower temperature.

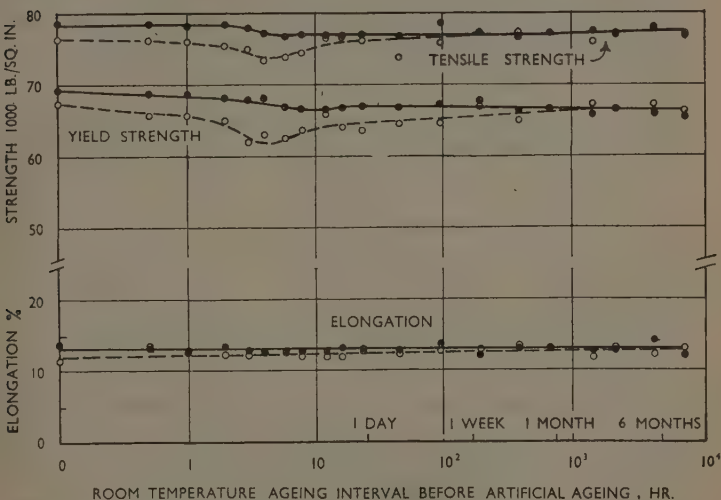
On this basis the effect is quite straightforward, but it is well established^{33, 35} that, although reversion at intermediate temperatures (150°–190° C.) will cause partial softening, subsequent re-hardening is then very markedly inhibited (see Fig. 6).

No explanations have been offered for this effect, and apparently it has not been the subject of any fundamental investigation. The rate of re-ageing may also be affected by the composition.³⁶

However, it is possible that the slow re-ageing after partial reversion may be explained along the following lines. Partial reversion will re-

dissolve the smaller G.P. zones leaving the larger unaffected. On subsequent room-temperature ageing the re-dissolved atoms may tend to join the small number of G.P. zones already present and form new small G.P. zones only very slowly. If this causes less total lattice strain, the apparent slowness of the re-ageing would be explained.

It is known that the properties after artificial ageing are sometimes affected by the period of natural ageing which elapsed after solution



[Courtesy American Society for Metals.]

Fig. 7.—The Effect of Room-Temperature Ageing Interval Before Artificial Ageing of an Aluminium-Zinc-Magnesium Alloy (Alcoa 75S) (Dix³⁸). 14 gauge \times grain specimens heat-treated for 20 min. at 870° F. (466° C.), and cold-water-quenched.

- Aged for 12 hr. at 275° F. (135° C.).
- " 24 " 250° F. (121° C.).

treatment. This effect has been noted in Al-Si-Mg-Cu (Alcoa 61S)³⁷ and Al-Zn-Mg alloys (Alcoa 75S)³⁸ (see Fig. 7). Both alloys give minimum properties when the interval at room temperature is about 1 day prior to their artificial ageing treatment at 160° C. in the first case, and 120°–135° C. in the second. After longer intervals at room temperature the properties after artificial ageing generally show a recovery. Similar effects have not been reported in wrought aluminium-copper or Al-Cu-Mg alloys, but it has been found that the rate of over-ageing is affected by the rate of heating to the ageing temperature.³⁹

The artificial ageing treatment for the Al-Zn-Mg alloys (Alcoa 75S)³⁸ was previously 24 hr. at 120° C. In order to save time a split ageing treatment has been recommended. This consists of 3 hr. at 120° C., cool to below 40° C., and 3 hr. at 165° C.,⁴⁰ which produces properties very similar to those obtained after 24 hr. at 120° C., and independent of the time at room temperature between quenching and artificial ageing.

On a very similar Al-Zn-Mg alloy (4.3% zinc, 2.5% magnesium), Wassermann⁴¹ found that the higher properties could be obtained on ageing at 150° C., if the alloy were first aged at 70° C., instead of immediately at 150° C. This is shown in Table I.

TABLE I.—*Tensile Properties Obtained on Al-Zn-Mg Sheet with Different Ageing Treatments.*⁴¹

Treatment	0.2% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Remarks
Aged immediately: 12 hr. at 150° C.	18.4	24.1	1.5 mm. sheet
Aged 2 days at 70° C., then 10 hr. at 150° C.	24.75	28.5	
3 months at room temperature, then aged 24 hr. at 120° C.	22.8	29.2	1.0 mm. sheet

These three types of behaviour under different treatments—partial reversion, natural ageing interval, and split ageing—are all examples of the way in which the G.P. zones already present* can materially influence the subsequent ageing. The split-ageing effects, such as Wassermann's, can probably be explained fairly simply. Both the number and the size of the "precipitate" (G.P. zones, coherent lattice, or true precipitate is covered here by this term) depend on the ageing temperature. Maximum properties are obtained when maximum lattice strain is present; this is produced by a large number of medium-sized particles corresponding, for example, to ageing at 120° C. of the Al-Zn-Mg alloy. Immediate ageing at a higher temperature probably leads to a smaller number of larger particles and lower total lattice strain. Ageing at a lower temperature, such as 70° C., will produce a larger number of smaller particles. If on ageing at 70° C. the majority of these have attained a size just above the critical size for stability and further growth at 150° C., they will continue to grow on transference to this higher temperature. Since they now exist in much greater numbers

* This makes the tacit assumption that natural ageing in Al-Zn-Mg alloys is due to the formation of G. P. zones, although this system has not yet been examined experimentally.

than would be the case with immediate ageing at 150° C., the total lattice strain may well reach a value close to, or above, that obtained at 120° C., and consequently full properties will be obtained.

An explanation of the effect of a short natural-ageing interval leading to a reduction in properties on artificial ageing is also possible on lines parallel to the effect of partial reversion. If ageing the Al-Zn-Mg alloy for 1 day at room temperature produces particles of "precipitate" of about the critical size for stability at 120° or 135° C., some of these will be re-dissolved on transference to this temperature. Precipitation on artificial ageing may occur preferentially on the small number that remain undissolved rather than form completely new nuclei, thus leading to lower total effective lattice strain.

The tentative explanations suggested above indicate that a thorough examination of reversion phenomena might give valuable information on precipitate size in relation to ageing temperature.

V.—CONCLUSIONS.

A study of age-hardening is essentially a study of nucleation and of the growth of the nuclei to a relatively small size, these structural changes covering the property alterations which are of greatest interest. A knowledge of the mode of formation, number, and growth of nuclei, and the factors influencing these, together with the build-up of attendant lattice strain, is most important from the viewpoint of age-hardening theory.

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SOME EFFECTS OF SILICON ON THE TENDENCY TO CRACKING IN ALUMINIUM-COPPER-MAGNESIUM ALLOYS OF HIGH PURITY.*

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SYNOPSIS.

In a previous investigation (*J. Inst. Metals*, 1948, **74**, 425) an examination was made of the effect of variation in the copper and magnesium contents on the tendency to cracking in aluminium-copper-magnesium alloys during welding. In the present work a study has been made of the effect of additions of silicon on the cracking of such alloys. It has been found that there is a marked progressive reduction in the susceptibility to cracking of alloys containing 2.5–4% copper and 0.5–1% magnesium with increase in the silicon content from 0.5 to 4%. Where aluminium-copper-magnesium-silicon alloys having copper and magnesium contents within these ranges are to be used for welding, it is suggested that the silicon content should be as high as practicable, of the order of 1.5%, consistent with successful heat-treatment, and that the copper content be maintained as high as is permissible within the specified range.

Certain of the alloys containing copper, magnesium, and silicon have been found to be susceptible to cracking at temperatures below the solidus in the restrained-weld test. It is not considered that cracking of this nature will occur to any marked extent in practical conditions of welding.

I.—INTRODUCTION.

In an earlier paper¹ a study was made of the effect of variation in the copper and magnesium contents on the tendency to cracking during and after solidification in welds in aluminium-copper-magnesium alloys of high purity. Many industrial alloys, among the most important of which are those of the Duralumin type, contain other elements which are present as impurities or are added for some specific purpose, in addition to copper and magnesium. Thus both iron and silicon are invariably present, but while the iron content is kept within reasonably low limits, the silicon content is frequently increased in order to improve the casting, ageing, and working properties of alloys of this type. It was therefore thought to be of interest to investigate the effect of additions of silicon on the tendency to cracking during welding of aluminium alloys containing copper and magnesium. The results of this investigation are recorded and discussed in the present paper. It is considered that the results are likely to be of value in the selection of Al-Cu-Mg-Si alloys suitable for welding.

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II.—PREVIOUS WORK.

There has been little systematic investigation of the effect of variations in composition on the tendency to cracking during the casting and welding of aluminium alloys containing copper, magnesium, and silicon, although there are numerous references in the literature to the welding properties of alloys of the Duralumin type. A number of investigators have reported that Duralumin is not suitable for welding,^{2, 3, 4} and that alloys of this type are very subject to cracking.⁵ Tichy,⁶ however, observed that by additions of silicon to an Al-Cu-Mg alloy prepared by remelting aircraft scrap, the originally poor casting properties of the alloy could be improved, and he developed an alloy containing principally 3% copper and 5% silicon which had good mechanical properties and was suitable for sand- or die-casting.

III.—EXPERIMENTAL WORK.

The methods used for determining the susceptibility to cracking of the alloys examined were the same as those employed in the previous investigation,¹ namely a ring-casting test and a restrained-weld test.

Ring-casting tests were carried out on 64 quaternary alloys containing up to 4% copper, 4% magnesium, and 4% silicon, the alloys being chosen to cover the range of marked tendency to cracking in the Al-Cu-Mg-Si system. All the alloys were made from super-purity aluminium, high-purity aluminium-silicon and aluminium-copper temper alloys, and virgin magnesium. The alloy field was covered by varying the percentage of one alloying element at a time while maintaining the percentages of the other two elements constant. The pouring temperature in the ring-casting test was standardized at 100° C. above the liquidus of the particular alloy considered, but as no information was obtainable from the literature on the liquidus temperatures of the quaternary alloys, these temperatures were determined by experiment.

In order to ascertain the degree of correlation between the results obtained in the ring-casting and restrained-weld tests, restrained-weld tests were carried out on a number of the alloys examined by the ring-casting test. Such tests were carried out on alloys containing equal amounts of copper and magnesium up to a total of 8% at constant silicon contents of 0.5, 1, and 2%, and up to a total of 4% at a silicon content of 4%.

The majority of the alloys for the welding tests were cast as slabs measuring $6\frac{1}{2} \times 4 \times \frac{9}{16}$ in., which were hot rolled at 420° C. to a thickness of 0.16 in. and cold rolled to the finishing thickness of 0.080 in. in the manner detailed in a previous paper.⁷ Those alloys which proved

difficult to hot roll were cast as slabs measuring $12 \times 4 \times \frac{9}{16}$ in., which were machined down to 0.32 in. in thickness before rolling. The rolling of these slabs was carried out in the cold, with frequent annealing at 420° C. followed by quenching from the annealing temperature.

With all the alloys the restrained-weld tests were made on material annealed for 1 hr. at 360° C. and slowly cooled from that temperature, and in all the tests welding was carried out in the direction of final rolling of the sheets. Several of the alloys examined by the restrained-weld test were found to be subject to cracking at temperatures below the solidus, such cracking occurring with some violence along the length of the weld when the temperature of the weld metal had fallen to about 200° C. In order to differentiate cracking at temperatures above the solidus from that occurring below the solidus, the first welds made under restraint in each alloy prone to this latter type of cracking were allowed to cool to room temperature in the restraining jig, while the remaining welds were removed from the jig when the weld metal was completely solid but before the onset of sub-solidus cracking.

As previously reported,¹ sub-solidus cracking can be differentiated from cracking which occurs at temperatures above the solidus by the difference in the appearance of the surface of the two types of fracture, and an examination was made of the surfaces of the cracks in representative samples of all the ring castings in order to determine the occurrence of the two types of cracking.

IV.—EXPERIMENTAL RESULTS.

The results obtained in the present ring-casting tests of the quaternary alloys have been combined with similar results obtained previously^{9, 10} for alloys in the systems aluminium-silicon, Al-Cu-Si, and Al-Mg-Si for the construction of Figs. 2-4. These Figures indicate the effect of variation in the copper and magnesium contents on the tendency to cracking in Al-Cu-Mg-Si alloys of constant silicon contents. The results obtained previously¹ in ring-casting tests of Al-Cu-Mg alloys free from silicon are recorded in Fig. 1.

The results of restrained-weld tests on aluminium alloys containing copper, magnesium, and silicon are plotted in Figs. 5 (a), (b), and (c), the results for the binary aluminium-silicon alloys being taken from the work of Pumphrey and Lyons.¹⁰

Although in the restrained-weld tests a considerable proportion of the alloys examined were found to crack at sub-solidus temperatures, only three alloys, namely those containing copper 4 + magnesium 4 + silicon 0.5%, copper 2 + magnesium 4 + silicon 1%, and copper 4 + magnesium 4 + silicon 1%, were found to exhibit sub-solidus

cracking in the ring-casting tests. The ranges of composition in which the two types of cracking occurred in the restrained-weld and ring-casting tests are indicated in Figs. 2-6.

It will be seen from Figs. 1-3 that the initial additions of silicon to aluminium alloys containing copper and magnesium cause a lowering of the copper and magnesium contents at which maximum cracking occurs. Addition of 2% silicon to Al-Cu-Mg alloys causes a marked reduction in cracking at temperatures above the solidus in all the alloys

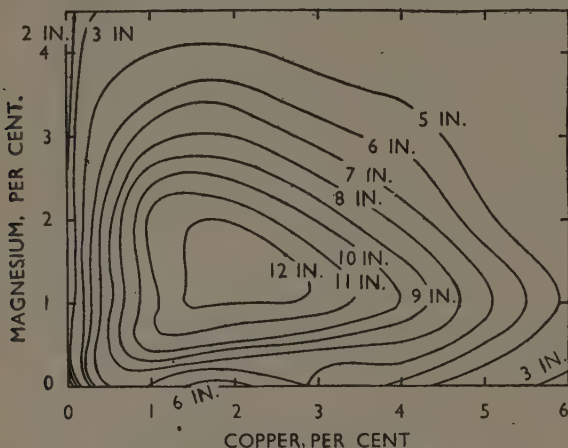


FIG. 1.—Cracking of Ring Castings in Al-Cu-Mg Alloys.

(Fig. 4). Increase in the silicon content to 4% caused the alloys to be completely free from cracking or to crack to a negligible extent at temperatures above the solidus.

The restrained-weld tests were carried out on a limited number of alloys containing equal amounts of copper and magnesium up to a total of 8% at silicon contents of 0.5, 1, and 2%, and up to a total of 4% at a silicon content of 4%. The curves in Figs. 5-6 indicate the degree of correspondence between the results of the restrained-weld and the ring-casting tests on this series of alloys. There is a greater tendency for cracking to occur at temperatures below the solidus in the alloys examined by the restrained-weld test than in the same alloys when examined by the ring-casting test, but otherwise the results of the two tests are in reasonable agreement as regards the compositions at which maximum cracking occurs. The precise forms of the cracking curves obtained in the two tests are, however, somewhat different.

Because of the complexity of the alloys and the apparent lack of reliable published information regarding the form of the constitutional diagram of the Al-Cu-Mg-Si system, it has not been found possible in this case to obtain any theoretical explanation for the variation of cracking at temperatures above the solidus with composition, as was obtained with other systems. The results of a microscopic

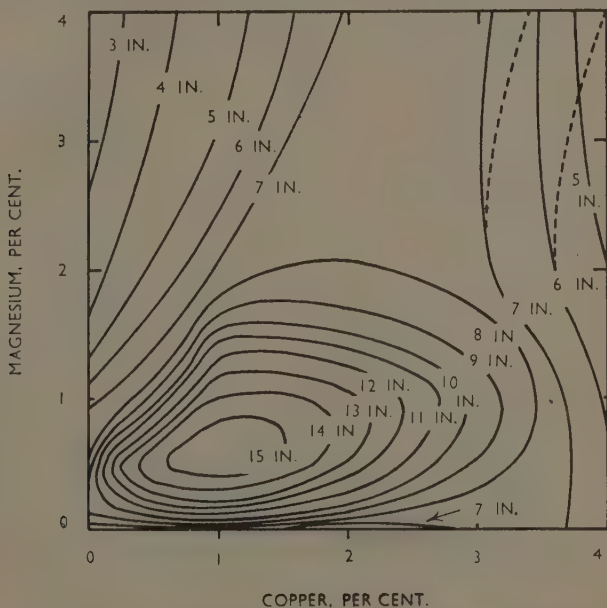


FIG. 2.—Cracking of Ring Castings in Al-Cu-Mg-Si Alloys Containing 0.5% Silicon.
 - - - - - Cracking contours when sub-solidus cracking is taken into account.

examination of the alloys prone to sub-solidus cracking, however, have confirmed the previous suggestion¹ that the tendency to sub-solidus cracking increases with increase in the completeness of the outlining of the crystal boundaries with intermetallic compound.

With increase in the total alloy content of the alloys examined, the welds in the restrained-weld tests had an increasing tendency to "sink through" and to allow of less reinforcement upon the upper surfaces. Apart from the tendency to cracking, however, no especial difficulty was encountered in welding any of the 18 alloys on which the restrained-weld tests were carried out, with the exception of the alloy containing copper

4 + magnesium 4 + silicon 0.5%, which, in addition to a pronounced tendency to superficial blistering in the vicinity of the weld bead during the welding operation, was found difficult to weld.

The materials containing more than 1.5% silicon with high copper and magnesium contents were very difficult to roll, and this reduced the possibility of extensive mechanical testing. Such mechanical test results as were obtained have been embodied in a previous paper.⁸

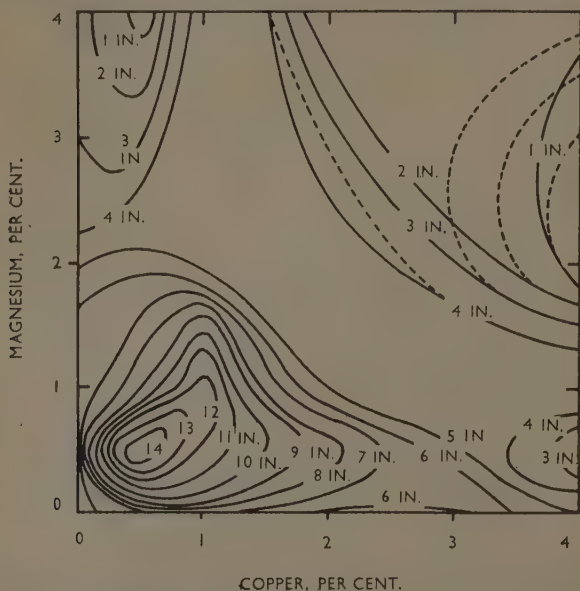


FIG. 3.—Cracking of Ring Castings in Al-Cu-Mg-Si Alloys Containing 1% Silicon.

----- Cracking contours when sub-solidus cracking is taken into account.

V.—PRACTICAL SIGNIFICANCE OF THE RESULTS.

Alloys of the Duralumin type normally contain, in addition to small amounts of other elements, between 2.5 and 4.5% copper and between 0.5 and 1% magnesium. The silicon content of such alloys is usually not more than 1%, and in most instances is kept below 0.7%. The diagram of cracking shown in Fig. 2 for Al-Cu-Mg alloys containing 0.5% silicon is therefore likely to be applicable to Duralumin-type alloys. From this diagram it is apparent that alloys containing copper

2.5-4, magnesium 0.5-1, and silicon 0.5% are very prone to cracking at temperatures above the solidus. The most susceptible alloy in this range is that containing copper 2.5, magnesium 1, and silicon 0.5%, and the alloy least liable to cracking is that containing copper 4, magnesium 0.5, and silicon 0.5%, the corresponding lengths of cracking in the ring-casting test being 12 and 6 in., respectively.

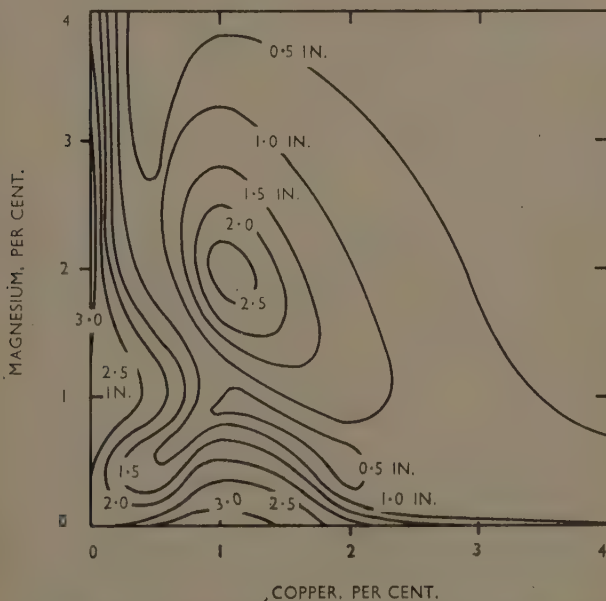


FIG. 4.—Cracking of Ring Castings in Al-Cu-Mg-Si Alloys Containing 2% Silicon.

Within this range of composition, the cracking contours of the diagram indicate that alteration of the magnesium content of any alloy produces little or no improvement in the susceptibility to cracking, but that increase in the copper content decreases this susceptibility. Although increase in the copper content from 2.5 to 4% causes a reduction from 12 to 6 in. in the length of cracking obtained in the ring-casting test, the lower figure still represents a marked susceptibility to cracking, and alloys in which the length of cracking in the ring-casting test is of this order would be expected to exhibit severe cracking during welding when the free contraction of the solidifying metal is restrained. Increase of the silicon content above 0.5% causes a progressive reduction

in the susceptibility to cracking of alloys containing 2.5-4% copper and 0.5-1% magnesium; thus, if Al-Cu-Mg-Si alloys having copper and magnesium contents within the above-specified ranges are required

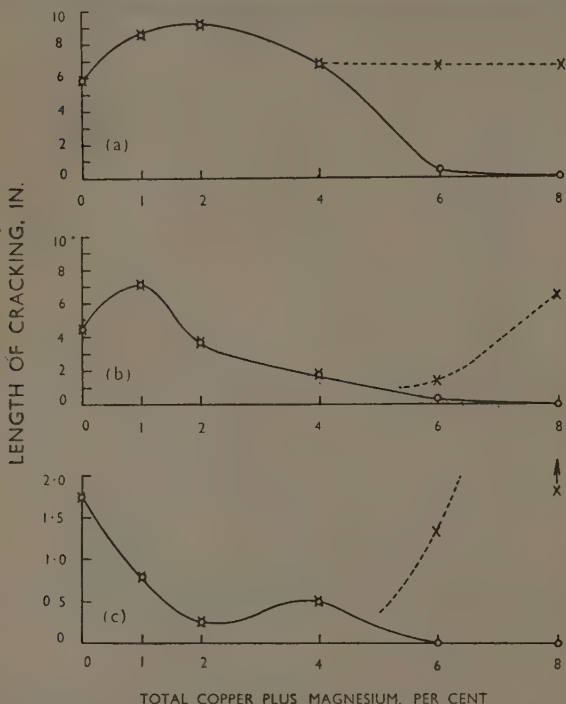


FIG. 5.—Cracking of Restrained Welds in Al-Cu-Mg-Si Alloys Containing: (a) 0.5%, (b) 1%, and (c) 2% Silicon, and Equal Amounts of Copper and Magnesium.
 × Cracking above and below the solidus.
 ○ Cracking above the solidus only.

for welding, it is suggested that the copper content be as high as possible within the compositional range and the silicon content as high as practicable, about 1.5%, bearing in mind the necessity for successful heat-treatment.

It should be noted, however, that in the present work no examination has been made of the effect of additions of elements such as iron, manganese, and titanium, and the presence of such elements in industrial alloys may have some effect on their tendency to cracking.

Although aluminium alloys containing copper, magnesium, and silicon have a marked susceptibility to cracking at temperatures below

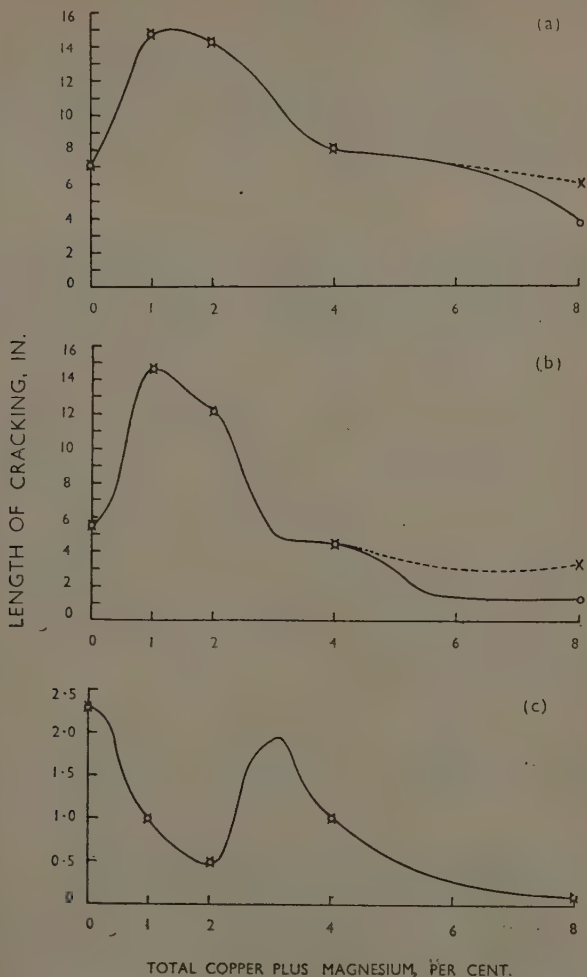


FIG. 6.—Cracking of Ring Castings in Al-Cu-Mg-Si Alloys Containing : (a) 0.5%, (b) 1%, (c) 2% Silicon, and Equal Amounts of Copper and Magnesium.

× Cracking above and below the solidus.

○ Cracking above the solidus only.

the solidus in the restrained-weld test, such cracking is unlikely to arise in practical conditions of welding, since, as mentioned in a previous paper,⁸ severe restraint of the contraction of a cooling weld at temperatures below the solidus can be avoided by careful design of the joint to be welded and by the employment of a suitable welding technique.

While the discussion above has been confined to the effect of additions of silicon on the tendency of Al-Cu-Mg alloys to crack during welding, it will be appreciated that the conclusions are also applicable to cracking during the casting of such alloys.

VI.—CONCLUSIONS.

Ring-casting tests have been carried out on 64 alloys and restrained-weld tests on 18 alloys to determine the effect of additions of up to 4% silicon on the tendency of Al-Cu-Mg alloys to crack during welding. The initial additions of silicon cause the region of maximum cracking in the Al-Cu-Mg cracking diagram to be moved to lower copper and magnesium contents, and further increase in the silicon content to 4% causes a progressive reduction in the tendency to cracking in all the alloys. Alloys containing 4% silicon are completely free from cracking or crack to a negligible extent at temperatures above the solidus.

Where Al-Cu-Mg-Si alloys containing 2.5–4% copper and 0.5–1% magnesium are to be used for welding, the silicon content should be about 1.5%, consistent with successful heat-treatment, and the copper content as high as is permissible within the specified range. Although certain of the alloys containing copper, magnesium, and silicon have been found to be susceptible to cracking at temperatures below the solidus in the restrained-weld test, it is considered that such cracking is unlikely to arise in practical conditions of welding.

ACKNOWLEDGEMENTS.

The work described was carried out under the general direction of Professor L. Aitchison, D.Met., for the Aluminium Development Association, by whose kind permission this paper is published.

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THE ANALYSIS OF CORROSION-TIME CURVES.*

1179

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SYNOPSIS.

Empirical corrosion-time curves usually conform to one of the four typical equations which may be termed rectilinear (1), parabolic (2), logarithmic (3), and exponential (4). Methods are available for accurate fitting of (1), (2), and (4), and a method is now given for (3) as an alternative to the approximation formerly used. The new method is particularly useful for relatively low rates of oxidation or corrosion.

I.—INTRODUCTION.

EMPIRICAL curves for the relation between the corrosion or oxidation y of metals and the time t of exposure usually conform to one of the following equations :

$$\text{The rectilinear equation : } y = k_1 t + k_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{The parabolic equation : } y^2 = k_1 t + k_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{The logarithmic equation : } y = k_1 \log (k_2 t + k_3) \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{The exponential equation : } y = k_1 [1 - e^{-k_2(t - k_3)}] \quad . \quad . \quad . \quad (4)$$

The units of the parameters k_1 , k_2 , k_3 are not similar for all four equations, but the suffixes 1, 2, and 3 have been used throughout for simplicity. The first three equations are generally recognized in relation to oxidation or corrosion, and have been discussed, for example, by Miley¹ and Evans.² The exponential equation has been observed under certain conditions with iron and zinc,^{3, 4, 5} and much more widely with aluminium and its alloys.^{6, 7}

The applicability of the rectilinear or parabolic equations, can be tested readily by plotting y or y^2 against t , and the value of the parameters can be determined from a straight line drawn to these points. The analysis of empirical data conforming to the exponential equation is more complex, but a reasonably simple method has been described elsewhere.^{7, 8} The fitting of experimental data to the logarithmic

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From the mean value of k_3 so determined we have :

$$k_2 = \frac{Ak_3}{B}$$

III.—APPLICATION OF NEW METHOD OF CALCULATION.

The avoidance of the trial-and-error technique is regarded as one advantage of the above method of fitting the logarithmic equation to experimental data. The main feature of the new method, however, is the provision for calculation of the value of the parameter k_3 . This feature of the method becomes more important as the value of k_2 becomes smaller, i.e. with lower rates of corrosion or oxidation. The careful measurements of the oxidation of zinc made by Vernon, Akeroyd, and Stroud⁹ may be used to illustrate this point.

The parameters of the logarithmic equation have been evaluated by the new method for the oxidation of abraded zinc at 100° C. with the following results :

$$k_1 = 0.164$$

$$k_2 = 0.00160$$

$$k_3 = 1.57$$

The values of y calculated with these parameter values are given in Table I, together with the calculated values (assuming $k_3 = 1.00$) and the observed values taken from the original paper.⁹

TABLE I.—*Re-Calculation of Weight Increments for Zinc at 100° C.*

Exposure Time t , hr.	Observed Values of y , mg./dm. ²	Calculated Values of y , mg./dm. ²	
		Taking $k_3 = 1.57$	Assuming $k_3 = 1.00$
24	0.110	0.109	0.120
45	0.135	0.136	0.156
71	0.165	0.163	0.184
119	0.203	0.204	0.218
183	0.249	0.247	0.246
240	0.287	0.277	0.266
283	0.290	0.297	0.276

The discrepancies between the final column of the Table and the observed values of y had been attributed⁹ to experimental errors becoming more important with the lower rates of oxidation at low temperatures. The values of y calculated by the new method, as given in the third column of the Table, indicate that the discrepancies were mainly due to the use of inaccurate parameter values in the calculations. This example illustrates the value of the new method under

the conditions which rendered calculations difficult with the alternative trial-and-error method.

With high initial rates of oxidation as obtained, for example, at higher temperatures, the trial-and-error method has given satisfaction⁹ because the accuracy of the value of k_3 is then relatively unimportant, while the new method is less useful for evaluating k_3 with high initial rates for the following reason. By taking $t = 0$ in equation (5) the initial rate of oxidation is given by:

$$\frac{dy}{dt} = \frac{1}{B} = \frac{k_1 k_2}{k_3}$$

Hence when the initial rate is high, e.g. at high temperatures, the value of B is small and therefore cannot be determined very accurately from equation (5). Indeed, assumption of unity is probably a better estimate of the value of k_3 than can be calculated from B when the initial rate is high.

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THE ELIMINATION BY LITHIUM OF BISMUTH EMBRITTLEMENT IN DEOXIDIZED COPPERS AND COPPER ALLOYS.* 1180

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SYNOPSIS.

Brittleness, which normally occurs in phosphorus-deoxidized bismuth-bearing coppers and copper alloys either at temperatures between 400° and 700° C. or after annealing within this temperature range, was overcome by the addition of lithium.

Of a number of elements including cerium, magnesium, and the alkali metals, which form compounds with bismuth, only lithium, when added in suitable amounts, was found to provide substantial freedom from embrittlement in notched-bar tests on non-arsenical bismuth-bearing copper. The optimum range of lithium contents for this purpose was defined, and the effect of lithium additions to deoxidized arsenical coppers and a number of copper alloys containing bismuth was also explored. The chemical method employed for the analytical determination of lithium in non-arsenical coppers is described in the Appendix, which includes a note on the spectrographic determination of lithium in all the coppers and alloys used.

The mechanism by which the addition of lithium can offset bismuth embrittlement was studied and is discussed. Evidence is provided to support the view that compound formation occurs between the two elements.

I.—INTRODUCTION.

CONCURRENTLY with a study of the mechanism of the embrittlement of phosphorus-deoxidized copper by bismuth¹ and an examination of the working behaviour of such coppers under laboratory and manufacturing conditions,² attention has been given to methods by which the embrittlement of deoxidized copper and copper alloys by bismuth may be overcome. No effective and readily applied means of removing small quantities of bismuth from fire-refined copper is available, and the present work deals with the possibility of converting the bismuth to a less harmful form by the addition of other elements which are themselves without detrimental effect on the properties of the coppers and alloys. The recommended procedure has been made the subject of a British Patent Specification, No. 581,903, of 21 May 1943.

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II.—PREVIOUS WORK.

Phosphorus-deoxidized coppers containing up to about 0.05% phosphorus may be severely embrittled by bismuth in the range of temperature from 400° to 700° C., or after heat-treatment in this range.¹

Bailey and Hallows³ have shown that high phosphorus contents tend to eliminate the embrittlement of copper by bismuth when testing is performed at room temperature after annealing between 400° and 700° C., but that the embrittlement at temperatures within this range is unaffected by the phosphorus content. Blazey⁴ independently showed the beneficial effect of excess phosphorus on the room-temperature properties of coppers containing bismuth, but did not test the materials at elevated temperatures. He also examined the effects of adding other elements to coppers containing bismuth and concluded, again from tests at room temperature, that: "In forged and drawn copper strips containing about 0.007% bismuth and up to about 1 at.-% of other elements, other than phosphorus, present singly, bismuth brittleness is present in those containing silver, zinc, aluminium, silicon, arsenic, antimony, chromium, manganese, iron, and nickel. Cadmium and tin, with some doubt as to the precise effect of chromium, alone appear to be able, like phosphorus, to reduce susceptibility to brittleness."

More recently, Voce and Hallows¹ examined non-arsenical coppers containing up to 0.1% bismuth and 0.4% phosphorus, and found, in confirmation of the earlier work on arsenical coppers,³ that the presence of sufficient phosphorus prevented embrittlement at normal but not at elevated temperatures. Micrographic examination showed that in the presence of such high phosphorus contents, the bismuth tended to occur in small pockets at grain corners, and there was no sign of the intercrystalline films which Schofield and Cuckow⁵ found in otherwise similar specimens of lower phosphorus content.

The beneficial effect of small amounts of phosphorus in overcoming the bismuth embrittlement of 70 : 30 or 60 : 40 brass has been described by Price and Bailey.⁶ An analogous effect, that of phosphorus in counteracting the embrittlement of 70 : 30 brass by antimony, has been described by Hull, Silliman, and Palmer,⁷ and recent work by McLean and Northcott⁸ on phosphorus and lithium additions to antimonial 70 : 30 brass has provided evidence of the formation of compounds between antimony and the addition elements.

III.—THE CHOICE OF ADDITION ELEMENTS.

It is shown later in the paper that additions of cadmium and tin, stated by Blazey ⁴ to reduce the susceptibility of copper to embrittlement by bismuth, are only effective, wholly or partially, at room temperature.

Following suggestions from Mr. W. L. Brown, of Cambridge University, and from Dr. Hume-Rothery, that cerium and magnesium might be useful additions, since they form compounds with bismuth, it was found from the literature that, in addition, compounds are formed between bismuth and the three alkali metals. The compositions and melting points of the five compounds are :

Bi_2Mg_3	833° C.
Bi_2Ce_4	1630° C.
BiLi_3	1145° C.
BiNa_3	775° C.
BiK_3	671° C.

To study the influence of these elements on the embrittlement of phosphorus-deoxidized non-arsenical copper containing bismuth, a series of melts was prepared, to which appropriate additions were made. The paper presents the results of notched-bar tests on these coppers and, in view of the beneficial effects of lithium on bismuth embrittlement which emerged from the work, further experiments are described on the addition of lithium to an extended range of materials containing bismuth; these include deoxidized arsenical and non-arsenical coppers and several copper alloys.

IV.—GENERAL EXPERIMENTAL DETAILS.

Most of the coppers and alloys were prepared from cathode copper, the others being made up from fire-refined bismuth-bearing copper ingots (containing 0.006% bismuth). The charges were melted under charcoal in salamander pots in a gas injector furnace.

The melts (with the exception of the brasses and aluminium bronzes) were first deoxidized with phosphorus, and sufficient time was allowed to elapse to ensure thorough deoxidation * before addition of the bismuth where required and alloying elements (if any) in that order. Crown Special zinc (99.99%), super-purity aluminium (99.99%), "Mellanear" tin (99.85%), and commercially-pure cadmium (99.9%) were used. The addition element, enclosed in copper foil within a hollowed salamander rod, was plunged beneath the surface of the melt. Lithium, magnesium, sodium, and potassium were added in elemental

* It has been shown ¹ that the degree of bismuth embrittlement is dependent upon the efficiency of deoxidation of the copper.

form, and cerium was used in the form of "Mischmetall" presumed to contain about 50% cerium. Sodium and potassium, which boil at temperatures of 878° and 758° C., respectively, had explosive effects when introduced into the molten copper.

Melts weighing approximately 10 lb. were chill cast into square-section bars, $8 \times 1.75 \times 1.75$ in., and rolled in one direction only. Unless otherwise stated, the bars were quenched from 850° C., cold rolled to 0.75 in. in four passes, annealed and quenched from 750° C., and cold rolled to 0.4 in. in two passes.

Notched-bar tests were made on the strips, using an Izod machine modified with a Charpy-type anvil; specimens $6 \times 1 \times 1$ cm. were taken from the strips parallel to the direction of rolling and notched at the centre with a British Standard Izod notch. The tests were made (i) at a temperature of 550° C. (in the middle of the brittle range for phosphorus-deoxidized copper containing bismuth) by rapid transference of the specimen from a muffle furnace to the anvil after holding it at this temperature for at least $\frac{1}{2}$ hr., and (ii) at room temperature, following annealing at 550° C. for $\frac{1}{2}$ hr. and quenching. Duplicate test values are given in most cases.

Similar notched-bar tests were made over a wider temperature range (i.e. at 350°, 450°, 550°, and 650° C.) on a few selected arsenical and non-arsenical coppers.

Analyses for lithium presented considerable difficulty, and the two methods used are described in the Appendix. The results obtained by the two methods were in reasonably good agreement, revealing residual lithium contents of the same order, as can be seen from Table IV. The chemical method was only satisfactory for non-arsenical coppers, but the spectrographic method was more versatile.

V.—RESULTS.

1. *Miscellaneous Addition Elements.*

The compositions of the coppers containing magnesium, cerium, sodium, and potassium with their notched-bar values are shown in Table I.

It will be seen that these four addition elements had practically no effect on the bismuth embrittlement.

2. *Lithium Additions.*

(a) *Non-Arsenical Coppers.*

The notched-bar values of the first coppers to which lithium was added, are given in Table II. An unusual difference occurred between

TABLE I.—Notched-Bar Values of Cold-Rolled Non-Arsenical Bismuth-Bearing Coppers Containing Magnesium, Cerium, Sodium, or Potassium.

Mark	Copper	Composition, %				Notched-Bar Value, ft.lb.			
		Bi	P	Other Elements		Annealed and Tested at 550° C.		Annealed at 550° C. and Quenched	
				Added	Residual (by chemical analysis)				
JXH128 *	Cathode	0.00004	0.035	71	76	115	103
JXH 17	Cathode	0.010	0.039	3	3	10	10
JXH 20	Cathode	0.011	0.047	0.013 Mg	0.01 Mg	3	3	12	13
JXH 21	"	0.011	0.035	0.013 Ce	trace Ce	3	4	11	11
JXH 50 †	"	0.011	0.043	0.035 Ce	0.032 Ce	5	5	18	18
JXH 40	Fire-refined ‡	0.0062	0.0078	0.055 Na	0.03 Na	3	3	5	5
JXH 43	"	0.0059	0.0066	0.055 K	0.02 K	3	4	4	4

* No bismuth addition.

† Hot rolled to 0.75 in. then cold rolled to 0.4 in.

‡ Containing 0.026% selenium and 0.006% tellurium.

some duplicate notched-bar values on account of slight cracking of the strips during cold rolling. The cracking was often only revealed by raggedness in the fracture of the specimens after testing, and where two values differ, the higher should be regarded as the more accurate, for reasons given in Section V. 2. (d), "General Observations", p. 753.

The cracking was overcome, except when using some of the highest lithium additions, by hot breaking down, to about 0.7 in., before cold rolling to a final thickness of 0.4 in., and the test values of further non-arsenical bismuth-bearing coppers treated with lithium and rolled by this schedule are given in Tables III and IV.

Lithium additions were found completely to eliminate the embrittlement of the copper by bismuth, both at 550° C. and on quenching from this temperature, and the materials in Table IV, all of which were made from cathode copper, were prepared to define the optimum range of residual lithium contents for the purpose. In coppers containing up to 0.01% bismuth with either 0.01 or 0.04% phosphorus, a residual lithium content of 0.01–0.02% was necessary to remove embrittlement at 550° C., whereas 0.005% was sufficient to render such coppers, with 0.04% phosphorus, ductile at room temperature. Thus, bearing in mind the tendency for cracking to increase with increasing lithium, the desirable range of lithium contents may be regarded as approximately 0.01–0.03%.

Lithium losses on addition to the copper were variable, but were

TABLE II.—The Effect of Lithium in Cold-Rolled Phosphorus-Deoxidized Non-Arsenical Coppers.

Mark	Copper	Composition, %		Notched-Bar Value, ft.lb.			Vickers Hardness Number (10-kg. load)			Grain-Size, $\sqrt{\text{Area}}$, mm.						
		Bi	P	Li		Annealed and tested at 550° C.	Annealed at 550° C. and Quenched	As- Rolled	Annealed 30 min. and Quenched		Annealed 30 min. and Quenched					
				Added	Residual (by chemical analysis)				550° C.	650° C.	750° C.	550° C.	650° C.	750° C.		
JXH128*	Cathode	0-00004	0-035	nil	...	71	76	115	103	109	55	52	53	0-02	0-025	0-05
JXH129	"	0-0051	0-034	nil	...	4	5	7	8	109	51	51	52	0-03	0-045	0-055
JXH 32	"	0-0053	0-044	0-0125	0-008 +	6	6	108	106	121	59	52	52	0-04	0-03	0-04
JXH 36	Fire- refined †	0-0055	0-011	0-015	0-012	4	5	43	29	114	49	49	48	0-025	0-03	0-03
JXH 33	Cathode	0-0049	0-044	0-035	0-016 +	42	52	98	115	120	81	59	54	0-015	0-02	0-02 (some 0-075)
JXH 37	Fire- refined †	0-0059	0-0096	0-035	0-019	66	39	59	78	114	56	51	47	0-025	0-025	0-045-0-09
JXH 41	"	0-0057	0-049	0-035	0-027	61	59	106	110	124	63	57	52	0-015	0-01	0-045-0-15
JXH 38	"	0-0058	0-0074	0-055	0-040	62	45	84	108	111	57	53	55	0-025	0-03	0-045-0-075
JXH 17	Cathode	0-0104	0-039	nil	...	3	3	10	10	109	63	43	49	0-05	about 0-1	0-09-0-15
JXH 34	"	0-0095	0-038	0-0125	0-006	16	18	113	113	123	71	48	45	0-05	0-04	0-12-0-8
JXH 22	"	0-0102	0-043	0-0125	0-008 +	6	5	105	104	121	59	44	51	0-06	0-07-0-17	0-07-0-17
JXH 35	"	0-0099	0-043	0-035	0-014 +	67	64	119	118	123	56	55	49	0-015	0-015	0-025-0-5

* No bismuth addition.

† For spectrographic determination, see Table IV.

‡ Containing 0-02% selenium and 0-008% tellurium.

TABLE III.—*Notched-Bar and Hardness Values of Phosphorus-Deoxidized Non-Arsenical Coppers Containing Bismuth and Lithium.*

Bars hot rolled at about 800° C. from 1.75 to 0.66 in. then cold rolled :
0.66 to 0.53 in.
0.53 to 0.4 in.

Small samples further reduced cold, without intermediate annealing :
0.4 to 0.315 in.
0.315 to 0.21 in.

Hardness determinations were made on the strips at the five thicknesses shown above.

Mark	Copper	Composition, %			Notched-Bar Value of 0.4-in. Strips, ft.lb.		Vickers Hardness Number (10-kg. load)			
		Bi	P	Li	Annealed at 550° C. and Quenched	Annealed and tested at 550° C.	Percentage Reduction			
							Nil	20	39	52
JXH45	Fire- refined *	0.006	0.044	nil	26	4	45	...	113	118
" 46	"	0.006	0.042	0.016	119	57	44	94	113	117
" 47	"	0.006	0.011	0.019	119	74	45	94	109	114
" 48	Cathode	0.0063	0.013	0.023	119	72	46	95	108	115
" 49	"	0.010	0.010	0.026	119	75	45	95	106	112
										68
										125
										123
										119
										121
										121

* Containing 0.026% selenium and 0.006% tellurium.

TABLE IV.—*Notched-Bar Values of Phosphorus-Deoxidized Non-Arsenical Coppers Containing Bismuth and Lithium.*

Mark	Composition, %					Notched-Bar Value, ft.lb.			
	Bi	P	Li			Annealed at 550° C. and Quenched		Annealed and Tested at 550° C.	
			Added	Residual					
				By Chemical Analysis	By Spectro- graphic Analysis				
KAV 71 *	0.00005	0.046	nil	111	116	69	71
KAV 91	0.0051	0.039	nil	...	n.d.	10	11	5	5
JXH 32 †	0.0053	0.044	0.0125	0.008	<0.005	108	106	6	6
JXH 33 †	0.0049	0.044	0.035	0.016	0.02	98	115	42	52
JXH 94	0.0055	0.042	0.055	0.026	0.015	113	109	64	65
JXH 95	0.0052	0.045	0.075	0.031	0.035	89	80	69	73
JXH 17	0.0104	0.039	nil	10	10	3	3
JXH 22 †	0.0102	0.043	0.0125	0.008	<0.005	105	104	6	5
JXH 35 †	0.0099	0.043	0.035	0.014	0.01	119	118	67	64
JXH 96	0.0100	0.046	0.055	0.023	0.02	102	72	71	68
JXH 97	0.0100	0.043	0.075	0.032	0.015	81	115	68	56
JXH 98	0.0100	0.012	0.025	0.017	0.01	109	115	65	63
JXH 99	0.0096	0.012	0.055	0.036	0.02	119	84	77	76
JXH100	0.0099	0.012	0.075	0.025	0.02	119	117	79	81

* No bismuth addition.

† Results from Table II; cold rolled materials.
n.d. = not detected.

sometimes as high as 70%, and it was not possible to introduce more than approximately 0.03% residual lithium into the copper.

Table II shows that lithium reduced the grain-size of the copper slightly, but calculations indicate that this is unlikely to be responsible for the improved properties of the lithium-bearing coppers. Assuming that the bismuth was not combined with lithium, but concentrated at the grain boundaries, the intercrystalline concentration in all the coppers is sufficient to cause serious embrittlement.¹ The mechanism of the lithium effect is discussed later (see Section V. 2. (e), p. 754).

The hardness values in Tables II and III show that, under the working and annealing conditions employed, lithium had no effect in increasing either the hardness of the coppers after annealing or the rate of hardening by cold work.

To examine the effectiveness of lithium in neutralizing bismuth embrittlement over a wider range of temperature, a few additional notched-bar tests were performed on three of the non-arsenical coppers at temperatures of 350°, 450°, 550°, and 650° C. The coppers, rolled hot and cold as before, were annealed beforehand at the respective testing temperatures until the lowest hardness values obtainable were reached, necessitating periods of 1050 hr. at 350° C., 100 hr. at 450° C.,

and 30 min. at 550° and 650° C. The notched-bar values, given in Table V, show some embrittlement at 350° and 450° C. in the coppers deoxidized with 0.04% phosphorus, although the one containing only 0.01% phosphorus was free from brittleness.

Specimens of the two higher-phosphorus coppers annealed for $\frac{1}{2}$ hr. at 550° C. were furnace cooled to 350° C., held at that temperature for a further $\frac{1}{2}$ hr., and then tested; the notched-bar values were 91 ft.lb. in each case.

TABLE V.—*Notched-Bar Values of Non-Arsenical Coppers at Temperatures from 350° to 650° C.*

Mark	Composition, %					Notched-Bar Value, ft.lb.							
	Bi	P	Li			Annealed and Tested at							
			Added	Residual									
				By Chemical Analysis	By Spectro-graphic Analysis								
350° C.	450° C.		550° C.		650° C.								
KAV71 *	0.00005	0.046	nil	94	...	83	...	69	71	54	58
JXH94	0.0055	0.042	0.055	0.026	0.015	31	31	40	30	64	65	63	62
JXH96	0.0100	0.046	0.055	0.023	0.02	17	28	66	81	71	68	46	47
JXH99	0.0096	0.012	0.055	0.036	0.02	105	94	93	...	77	76	66	65

* No bismuth addition.

(b) *Arsenical Coppers.*

The arsenical coppers were worked by the hot and cold rolling schedule ultimately adopted for the non-arsenical coppers.

The results in Table VI show that lithium has a marked beneficial effect in deoxidized arsenical coppers containing bismuth, although the effect of the bismuth is not entirely eliminated; the lithium losses were higher than in the non-arsenical coppers, but the results do not suggest that higher lithium contents would be more effective.

The presence of about 0.02% lithium in arsenical copper containing 0.003% bismuth raised the notched-bar values at 550° C. to 40% and at room temperature to 75% of those of the "bismuth-free" copper; with a similar lithium content but with 0.006% bismuth, the recovery at 550° C. was slightly less.

The optimum notched-bar values of between about 25 and 35 ft.lb. obtained for the lithium-treated coppers tested at 550° C. represent a great improvement on values of 3 and 6 ft.lb., given by the corresponding lithium-free coppers containing 0.006 and 0.0035% bismuth, respectively. Thus, although lithium does not neutralize bismuth embrittlement in deoxidized arsenical coppers to the complete degree

TABLE VI.—*Notched-Bar Values of Phosphorus-Deoxidized Arsenical Coppers Containing Bismuth and Lithium.*

Mark	Copper	Composition, %					Notched-Bar Value, ft.lb.			
		Bi	P	As	Li		Annealed at 550° C. and Quenched		Annealed and Tested at 550° C.	
					Added	Residual (by spectrographic analysis)				
KAV121 *	Cathode	0.0001	0.040	0.36	nil	...	106	116	80	77
KAV127	Cathode	0.0035	0.043	0.33	...	n.d.	34	36	6	6
JXH101	"	0.0034	0.008	0.39	0.03	<0.005	61	52	19	18
JXH102	"	0.0033	0.009	0.37	0.05	0.02	79	74	33	32
JXH103	"	0.0033	0.011	0.42	0.10	0.015	75	79	35	34
JXH 51	Fire-refined †	0.0062	0.017	0.40	nil	...	9	9	3	4
JXH 53	"	0.0064	0.015	0.36	0.03	<0.005	45	48	4	4
JXH 54	"	0.0064	0.015	0.40	0.05	0.015	72	70	20	23
JXH 69	Cathode	0.0057	0.0068	0.45	0.05	0.006	88	81	24	26
JXH 68	Fire-refined †	0.0073	0.0096	0.44	0.10	0.02	63	57	19	22

* No bismuth addition.

† Containing 0.026% selenium and 0.006% tellurium.

n.d. = not detected.

TABLE VII.—*Notched-Bar Values of Arsenical Coppers at Temperatures from 350° to 650° C.*

Mark	Composition, %					Notched-Bar Value, ft.lb.							
	Bi	P	As	Li		Annealed and Tested at							
				Added	Residual (by spectro- graphic analysis)								
						350° C.		450° C.		550° C.		650° C.	
KAV121 *	0.0001	0.040	0.36	nil	...	108 †	...	93 †	...	80	77	64	66
JXH102	0.0033	0.009	0.37	0.05	0.02	49	45	42	43	33	32	33	30
JXH 69	0.0057	0.0068	0.45	0.05	0.006	11	11	18	18	24	26	28	24

* No bismuth addition.

† By extrapolation from higher-temperature values.

experienced in non-arsenical coppers, it does, nevertheless, effect a major improvement.

Notched-bar tests (Table VII) on two of the lithium-treated arsenical coppers at temperatures of 350°, 450°, 550°, and 650° C., after annealing at the respective testing temperatures for the same periods of time as defined for the non-arsenical coppers (p. 748), indicated rather severe embrittlement of the copper of higher bismuth content at 350° C.; this copper contained about 0.006% lithium. The same copper an-

nealed for $\frac{1}{2}$ hr. at 550° C. was furnace cooled to 350° C., held for $\frac{1}{2}$ hr. at this temperature and tested, giving a notched-bar value of 41 ft.lb.

(c) Copper Alloys.

Hot breaking down was not practicable for the bismuth-bearing alloys without lithium, and consequently all the alloys were reduced by cold rolling following initial quenching from 850° C. according to the schedule described in Section IV.

(i) *Cadmium Coppers* (1% Cadmium).—A series of melts was prepared from cathode copper, and the results given in Table VIII show that with about 0.006% bismuth, lithium contents of approximately 0.005–0.015% completely restored the room-temperature notched-bar values (quenched from 550° C.) and raised the value at 550° C. from 4 ft.lb. to approximately 25 ft.lb. (compared with nearly 90 ft.lb. for the bismuth-free alloy). In the presence of only 0.003% bismuth, 0.015% lithium increased the notched-bar value at 550° C. to approximately 50 ft.lb., and again restored the full value at room temperature following quenching. Higher lithium contents were not more beneficial with either bismuth content.

The addition of lithium to bismuth-bearing cadmium copper and deoxidized arsenical copper is thus similar in effect. Although lithium in both these alloys does not completely remove bismuth embrittlement, it reduces its severity, resulting in notable increases in the notched-bar values.

TABLE VIII.—*Notched-Bar Values of 1% Cadmium Coppers Containing Bismuth and Lithium.*

Mark	Composition, %					Notched-Bar Value, ft.lb.			
	Bi	P	Cd	Li		Annealed at 550° C. and Quenched		Annealed and Tested at 550° C.	
				Added	Residual (by spectrographic analysis)				
JXH 66 *	0.0004	0.012	1.11	nil	...	119	119	89	88
JXH104	0.0031	0.012	1.04	0.03	0.015	105	110	45	57
JXH105	0.0032	0.012	1.02	0.05	0.04	98	103	42	45
JXH106	0.0031	0.012	0.86	0.10	0.065	93	98	26	24
JXH 55	0.0055	0.014	1.12	nil	n.d.	61	62	4	4
JXH560	0.0059	0.012	1.17	0.01	<0.005	119	119	23	24
JXH 57	0.0060	0.012	1.16	0.03	0.015	111	119	23	29
JXH 58	0.0055	0.012	1.17	0.05	0.025	119	117	20	20

* No bismuth addition.

n.d. = not detected.

(ii) *Tin Bronzes (5% Tin).*—A series of 5%-tin bronzes was prepared from cathode copper and the results in Table IX show that the addition of approximately 0.006% bismuth reduced the notched-bar value of the bronzes from 25 to 4 ft.lb. at 550° C., although the specimens quenched from 550° C. showed undiminished toughness. The presence of about 0.01% lithium, however, restored the values at 550° C. substantially to those given under the same conditions by the bismuth-free alloy. Increasing the lithium content to 0.03% gave less favourable results.

TABLE IX.—*Notched-Bar Values of 5%-Tin Bronzes Containing Bismuth and Lithium.*

Mark	Composition, %					Notched-Bar Value, ft.lb.			
	Bi	P	Sn	Li		Annealed at 550° C. and Quenched		Annealed and Tested at 550° C.	
				Added	Residual (by spectrographic analysis)				
JXH70*	0.0007	0.0070	4.93	nil	...	114	108	24	25
JXH59	0.0066	0.0077	4.70	nil	n.d.	119	119	4	4
JXH61	0.0059	0.010	4.92	0.03	0.008	119	118	21	21
JXH62	0.0062	0.010	4.64	0.05	0.033	78	85	12	12

* No bismuth addition.

n.d. = not detected.

(iii) *70 : 30 Brass.*—Alloys were prepared from cathode copper and pure zinc, and it is seen from the results in Table X that although specimens quenched from 550° C. and tested at room temperature were little affected by the presence of approximately 0.007% bismuth, tests at 550° C. showed extreme brittleness at this temperature. A lithium content of 0.02% restored the notched-bar value of the alloy to that of the control specimens.

TABLE X.—*Notched-Bar Values of 70 : 30 Brass Containing Bismuth and Lithium.*

Mark	Composition, %					Notched-Bar Value, ft.lb.			
	Bi	Cu	Zn †	Li		Annealed at 550° C. and Quenched		Annealed and Tested at 550° C.	
				Added	Residual (by spectrographic analysis)				
JXH71*	0.0005	69.84	30.16	nil	...	93	104	34	34
JXH64	0.0067	69.90	30.10	nil	n.d.	86	72	3	4
JXH72	0.0070	69.97	30.03	0.03	0.02	97	98	32	32

* No bismuth addition.

† By difference.

n.d. = not detected.

(iv) 5%-Aluminium Bronzes.—The results of notched-bar tests on 5%-aluminium bronze alloys, prepared from cathode copper and deoxidized with 0.5% manganese, are given in Table XI.

TABLE XI.—Notched-Bar Values of 5%-Aluminium Bronzes Containing Bismuth and Lithium.

Mark	Composition, %						Notched-Bar Value, ft.lb.			
	Bi	Cu	Al †	Mn	Li		Annealed at 550° C. and Quenched		Annealed and Tested at 550° C.	
					Added	Residual (by spectrographic analysis)				
MPL1 *	0.0001	94.37	5.12	0.51	nil	...	109	...	32	31
MPL2	0.0054	94.43	5.07	0.49	nil	n.d.	58	64	6	6
MPL3	0.0056	94.40	5.10	0.49	0.03	...	118	119	35	36
MPL4	0.0054	94.38	5.16	0.45	0.05	0.008	119	119	37	39

* No bismuth addition.

† By difference.

n.d. = not detected.

The addition of 0.005% bismuth to the lithium-free alloy produced severe embrittlement at 550° C., and, compared with the "bismuth-free" standard, halved the notched-bar value at room temperature after quenching. The lithium additions completely counteracted the effect of the bismuth, and when about 0.01% lithium was present the test values were superior to those of the standard alloy.

(d) General Observations.

The studies of earlier workers on lithium coppers are summarized by Osborg⁹ in a treatise on lithium. He reports that "all the investigators come to the same conclusion, namely, that lithium is an excellent deoxidizer and refining agent for copper".

The use of lithium to overcome bismuth embrittlement in the coppers and alloys described in this paper increased their apparent viscosity to some extent, particularly when the larger amounts of lithium were used. The presence of lithium in the metal gave rise to the formation of an oxidized "scum" on the surface of the molten stream during pouring and enveloping the stream in a coal-gas flame did not prevent formation of this film. It is therefore of the greatest importance that the lithium additions be kept to a minimum, since the presence of this oxidized film may have been partly responsible for the localized cracking, found to be most prevalent in the cold-rolled non-arsenical coppers, but sometimes only detected when the cracks opened up at or near the fracture of a notched-bar specimen. Although hot rolling in the initial stages of reduction appeared to overcome this

defect almost entirely, a similar tendency to crack was noted under these conditions in the non-arsenical coppers to which the highest lithium additions were made, and, to a much lesser degree, in the form of slight raggedness of fracture, in a few of the arsenical coppers. A few of the alloy specimens also revealed the defect.

It will be seen that an increase of lithium content over that required to overcome the bismuth embrittlement, either completely or to the fullest extent possible, usually resulted in inferior test values, indicating that lithium itself has an embrittling influence when used in excess. In the present experiments, phosphorus has been added in most cases in order to deoxidize the copper or alloy before the lithium addition, otherwise unknown amounts of lithium would have been used in deoxidation, and it would not have been possible to control the effective lithium addition.

(e) *Mechanism of the Effect.*

It is possible that the elimination of bismuth embrittlement by lithium additions is due to formation of the stable compound BiLi_3 , which has a melting point of 1145°C. , notwithstanding the fact that cerium, magnesium, potassium, and sodium, which also form stable compounds with bismuth, were ineffective. However, the melting points of the various compounds are only a very rough guide to the affinities of the addition elements for bismuth, and the extent to which such compound formation occurs is also dependent on the affinity of the addition element for other elements in the coppers, including the copper itself. It may be significant that no stable compounds are formed in the copper-lithium system, but fairly high-melting-point compounds occur in the systems copper-cerium and copper-magnesium; no information is available for the copper-sodium and copper-potassium systems. Pursuing the same rough indication of affinities, the systems formed by lithium with arsenic, tin, aluminium, zinc, and cadmium, respectively, all contain stable compounds; no information is available for lithium-phosphorus. It might be expected therefore that if lithium eliminates bismuth embrittlement by converting the bismuth to an insoluble stable compound, the lithium addition would be less effective in the copper alloys with arsenic, tin, aluminium, zinc, and cadmium. The experimental results show that in two alloys of the five this is the case.

To determine whether or not a lithium-bismuth compound was likely to be formed in the coppers, a non-arsenical copper with high bismuth and lithium contents (0.072% bismuth, 0.06% lithium), and without phosphorus, was prepared for metallographic study; the material was made by

FIG. 1.—Copper Containing 0.072% Bismuth, 0.06% Lithium, after Cold Hammering and Annealing at 550° C. Electrolytically polished. $\times 100$.

FIG. 2.—Same Alloy as in Fig. 1. Unetched. $\times 2500$.

FIG. 3.—Same Field as Shown in Fig. 2. Etched with dilute ferric chloride. $\times 2500$.

FIG. 4.—Copper Containing 0.039% Lithium, after Transfer of Bismuth from Copper of High Bismuth Content. $\times 500$.

[To face p 754.]

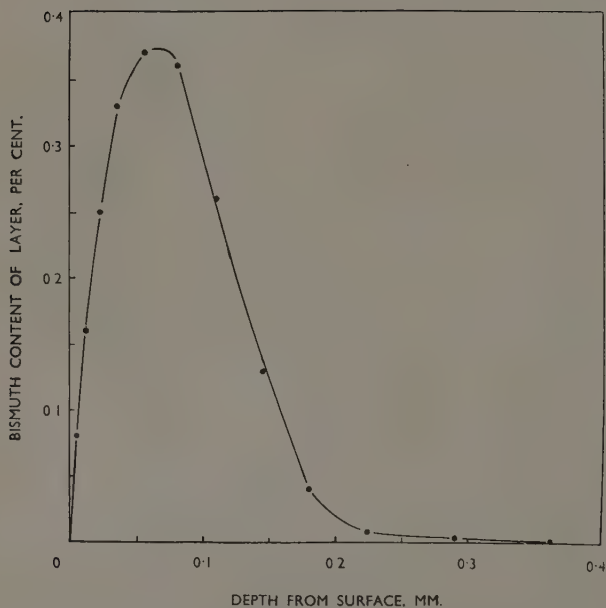


FIG. 5.—Bismuth Content of Surface Layers of Lithium-Deoxidized Copper after Bismuth Transfer.

melting oxygen-free copper, bismuth, and lithium in a silica boat within a tube furnace through which a stream of argon was flowing. After cooling, the copper was malleable on cold hammering and, after working, was annealed for 1 hr. at 550° C. and quenched. Fig. 1 (Plate C) illustrates the structure after electrolytic polishing in phosphoric acid (33% by volume); bismuth films, of the type shown by Schofield and Cuckow⁵ to be revealed by this etching treatment, could not be detected, although chains of globules were seen. Fig. 2 (Plate C) which is an unetched structure at higher magnification, shows that the globules, having the characteristic blue colour of bismuth, each contain a darker particle, which may be BiLi_3 . The globules follow the interdendritic pattern of the original cast structure and are unrelated to the recrystallized grains. Fig. 3 (Plate C) shows the same field after etching in ferric chloride; a structure characteristic of bismuth after this etching treatment has been developed in the lighter areas of the globules.

In a further experiment, a bismuth-free copper containing 0.039% lithium was heated in proximity to a phosphorus-deoxidized copper containing 0.075% bismuth and thereby exposed to bismuth vapour. The specimens were in the form of strips 0.03 in. thick, and the lithium copper was sandwiched between two strips of the bismuth copper and wrapped in a closed packet of phosphorus-deoxidized copper foil before heating for 8 hr. at 750° C. in a bright-annealing atmosphere. The foil packet was quenched from this temperature and the lithium copper was examined micrographically and by layer analysis. Fig. 4 (Plate C) shows a section through the surface layers of the strip, perpendicular to the rolled face, and reveals chains of blue globules at grain boundaries at a short distance beneath the surface; the globules were of the characteristic blue colour shown by bismuth and again appeared to contain darker particles. The maximum concentration of the blue constituent appeared about 0.08 mm. below the surface. Layer analysis of the specimen for bismuth gave the results shown in Fig. 5 (Plate CI), from which it can be seen that the concentration of bismuth rose to a maximum until a point approximately 0.07 mm. from the surface was reached.

Thus, the maximum concentrations of bismuth and of blue constituent were found to occur at a similar distance below the surface. In this region, the bismuth concentration in the recipient was much greater than in the original donor, and this condition could only have been attained by precipitation of bismuth from solution as a compound in the lithium-bearing copper. This provides strong evidence that the blue constituent in this specimen was a compound, such as BiLi_3 , and not bismuth.

It is concluded, therefore, that lithium eliminates bismuth embrittlement from copper and its alloys by forming an insoluble compound with the bismuth. It has been shown, however, that coppers given an unusual annealing treatment, i.e. very long times at comparatively low temperatures (350° and 450° C.), may show slight bismuth embrittlement despite the presence of lithium in amount sufficient to eliminate the embrittlement from specimens annealed at higher temperatures. A tentative explanation for these results is that some or all of the bismuth was in solid solution in the coppers prior to cold rolling and annealing for test. It is then supposed that the bismuth is precipitated as harmless inclusions of the compound during annealing at 550° C., but that at lower temperatures, where the solute atoms are less mobile, the bismuth is not all fixed in this way, and some of it forms harmful grain-boundary films rather than a compound with the lithium.

VI.—SUMMARY OF RESULTS.

It has been shown that bismuth and lithium may form a compound, possibly BiLi_3 , the presence of which will overcome, to a greater or lesser extent, the embrittling effect of the bismuth in the uncombined state. The efficiency of the lithium in this respect is dependent on the copper or alloy under consideration, but when added in controlled amounts this element will, in certain instances, neutralize bismuth embrittlement both at elevated temperatures and at room temperature after annealing.

The results may be summarized as follows :

(1) *Non-Arsenical Coppers*.—The effects of up to 0.01% bismuth were neutralized by the presence of 0.01–0.03% lithium, equally good results being obtained whether 0.01 or 0.04% phosphorus was used as an initial deoxidant.

(2) *Arsenical Coppers*.—Bismuth embrittlement was less completely removed than in non-arsenical coppers. The maximum bismuth content used was 0.006–0.007% and, following initial deoxidation with phosphorus, a residual lithium content of about 0.02% effected a most useful improvement in ductility.

(3) *Cadmium Coppers* (1% *Cadmium*).—The ductility of cadmium copper containing up to 0.006% bismuth was notably improved by the addition of lithium, although the embrittlement was not completely removed; the optimum lithium content was about 0.015%.

(4) *Tin Bronzes* (5% *Tin*).—The embrittling effect of 0.006% bismuth was overcome by the presence of approximately 0.01% lithium.

(5) 70 : 30 *Brass*.—The brittleness caused by 0.007% bismuth was neutralized by about 0.02% lithium.

(6) *Aluminium Bronzes* (5% *Aluminium*).—Lithium of the order of 0.01% in alloys containing approximately 0.006% bismuth gave notched-bar values higher than those of the "bismuth-free" bronze.

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APPENDIX.

THE ESTIMATION OF LITHIUM IN COPPER.

1. *Chemical Method.*

The chemical method used for non-arsenical coppers containing small amounts of bismuth and phosphorus, but otherwise of high purity, involved removal of the bulk of the copper electrolytically in nitric acid solution, followed by removal of remaining Group IIA elements with hydrogen sulphide in hydrochloric acid solution. The resulting solution was taken to dryness, a small amount of sodium chloride added, and the lithium chloride extracted from the residue with hot amyl alcohol. The extract was taken to dryness, and the lithium chloride residue was converted to sulphate for weighing. Sodium chloride is slightly soluble in the alcohol and a small correction was necessary.

Analyses of synthetic solutions prepared by adding 0.05% lithium as a standardized lithium chloride solution to one of phosphorus-deoxidized copper (0.035% phosphorus) containing bismuth (0.01%) gave the following results:

1. 0.051%.
2. 0.049%, 0.048%.

Determinations on samples of phosphorus-deoxidized coppers containing small amounts of bismuth gave the following percentages of lithium :

Sample 1 :	0.015%, 0.014%.
„ 2 :	0.037%, 0.040%.
„ 3 :	0.015%, 0.017%.
„ 4 :	0.033%, 0.038%.
„ 5 :	0.024%, 0.025%.
„ 6 :	0.012%, 0.010%.

The method was designed only for non-arsenical coppers containing small amounts of bismuth and phosphorus. Other elements, whose chlorides are soluble in amyl alcohol, would cause interference unless completely removed before the extraction, and the spectrographic method outlined below was therefore used for the arsenical coppers and copper alloys.

2. *Spectrographic Method.*

Lithium contents down to 0.005% were determined spectrographically by a solution method. Approximately 0.1 c.c. of a 50% nitric acid solution * of the sample (100 g. metal/l.) was loaded into a pure copper cup, 5 mm. in dia. and 6 mm. deep, and sparked against a 5-mm.-dia. pure copper rod, using the B.N.F. General-Purpose Source Unit set to give arc-like excitation.

Synthetic standard solutions with known lithium additions were photographed on the same plate. The lithium line, 6707.8 Å, and the neighbouring background were microphotometered and the spectra evaluated in the usual way. In the range 0-0.06% lithium, contents differing by 0.005% lithium were readily distinguished, and the reproducibility of results was of this order.

* The tin bronze was dissolved in an acid mixture consisting of 1 part HCl, 4 parts HNO₃ and 5 parts water.

AN EXPERIMENTAL INVESTIGATION BY A 1181 DYNAMICAL METHOD OF THE VARIATION OF YOUNG'S MODULUS WITH TEMPERATURE.*

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SYNOPSIS.

This paper describes a method for the determination of the variation of Young's modulus with temperature for metals and alloys, in which the specimen, in the form of a fixed-free bar about 2.5 cm. long, is maintained in transverse vibration by the action of superposed steady and alternating magnetic fields. Resonance of the bar is detected by transmitting its vibration to a gramophone pick-up whose output is amplified, rectified, and applied to a galvanometer. The ratio of Young's modulus at any two temperatures is shown to be approximately equal to the square of the ratio of the two corresponding natural frequencies of the bar in the fundamental mode and in zero magnetic field. A small correction factor for the thermal expansion of the material is discussed. Young's modulus-temperature curves are reproduced for commercial brass, copper, mild steel, iron, nickel, cobalt, Monel metal, Ferry, iron-48% nickel alloy, β brass, and copper-gold alloy. The discontinuities in these curves are discussed and the results compared with those of previous investigators. The accuracy of the results is considered, and the advantages of the method over existing methods indicated.

I.—INTRODUCTION.

THE work described in the present paper was carried out between 1938 and 1940, and its aim was to evolve an accurate method for determining the variation with temperature of Young's modulus of metals and alloys. The experimental method devised, which involves the measurement of the natural frequency of transverse vibration of a fixed-free bar of the test material, is a development of that described by Davies and James^{1,2} for the measurement of Young's modulus at room temperature. The measurement under consideration presents many difficulties for any but small ranges near room temperature, and most of the methods employed prior to about 1933^{3,4,5} are difficult to apply over an extended temperature range. In recent years, however, a number of authors have published descriptions of apparatus for the determination of Young's modulus, by various dynamical methods⁶⁻¹² which possess important advantages over static methods. The specimens may be excited by piezo-electric, electromagnetic, electrostatic, or magnetostrictive

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methods,¹³ and the vibration produced may be either transverse or longitudinal.

In the present work, the specimen is set into transverse vibration electromagnetically. This demands a specimen in the form of a bar only about 2.5 cm. long, the temperature of which may be raised uniformly without undue difficulty while still being able to detect its resonant condition.

II.—THEORY OF METHOD.

1. *The Fixed-Free Loaded Bar.*

The behaviour of a bar clamped at one end and loaded at the free end has been investigated by one of the authors,¹⁴ when both the bar and load have finite dimensions, the rotatory inertia of the load and the bar and the shearing of the elements of the bar being taken into consideration. If:

ρ = density of the material of the bar;

l = vibrating length of the bar;

σ = thickness of the bar;

c = ratio of mass of load to that of bar;

k = radius of gyration of cross-section of bar about an axis through the centre of gravity, perpendicular to the plane of motion;

K = radius of gyration of the load about an axis through its point of attachment to the bar, perpendicular to the plane of motion;

N_0 = resonant frequency of loaded bar;

then the Young's modulus E of the material of the bar is given by :

$$E = \frac{48\pi^2\rho l^4 N_0^2}{\sigma^2(Z^4 + D)} \quad \dots \quad (1)$$

in which :

$$Z^4 = \frac{210}{8c+1} \left\{ (4c+1) - \left[16c^2 + \frac{31}{35}(8c+1) \right]^{\frac{1}{2}} \right\}$$

and D , the total correction factor for rotatory inertia and shear, is given by :

$$D = - \frac{12a + Z^4(A'b - B'a)}{A'\sqrt{(B'^2 - 4A'/35)}}$$

where :

$$A' = 1 + 8c$$

$$B' = 1 + 4c$$

$$a = 168d(1 + 2.5c) + 56\beta^2(1 + 3c + 15d) \\ + 56\epsilon\beta^2(1 + 6c + 45d + 90cd)$$

$$b = 12d + 6\beta^2 + 6\epsilon\beta^2 (1 + 2c)$$

$$d = \frac{cK^2}{l^2}$$

$$\beta = \frac{k}{l}$$

$$\epsilon = \frac{R \cdot E}{G}$$
, where G is the rigidity modulus of the material of the bar and R is a numerical, non-dimensional constant depending on the shape of the cross-section of the bar; for a rectangular cross-section, R equals 1.2.

From equation (1), if E_1 and E_2 denote the values of Young's modulus at temperatures t and $(t + \theta)^\circ \text{C.}$, respectively :

$$\frac{E_2}{E_1} = \frac{N_{02}^2 Z^4 + D_1}{N_{01}^2 Z^4 + D_2} \cdot (1 + \alpha\theta)^{-1} \quad \dots \quad (2)$$

in which N_{01} , D_1 and N_{02} , D_2 are the values of N_0 and D at temperatures t and $(t + \theta)^\circ \text{C.}$, respectively, and α is the mean coefficient of linear expansion of the bar in the range t to $(t + \theta)^\circ \text{C.}$

(a) *Variation of D with Temperature.*

The factor D is a function of c , β , d , and ϵ , the first two of which are clearly independent of temperature. d may also be taken as independent of temperature, and for a typical test bar it may be shown that variations of ϵ with temperature, if neglected, will introduce an error of less than 0.1%.

(b) *The Factor $(1 + \alpha\theta)^{-1}$.*

The magnitude of this factor, taking into consideration the variation of α with temperature, may be illustrated by reference to nickel, for which full data are available.¹⁵ In this case, the factor is about 0.99 when θ is 600°C. , while the difference in its values, when mean and actual values of α are taken, amounts to less than 0.2%.

It follows from equation (2) that the ratio of Young's modulus at $T^\circ \text{C.}$ to that at room temperature, $R^\circ \text{C.}$, is :

$$\frac{E_T}{E_R} = \frac{N_{0T}^2}{N_{0R}^2} [1 - \bar{\alpha} (T - R)],$$

where N_{0R} , N_{0T} are the fundamental natural frequencies of transverse vibration of the specimen at $R^\circ \text{C.}$ and $T^\circ \text{C.}$, respectively, and $\bar{\alpha}$ is the mean coefficient of linear expansion of the material in the range $R^\circ \text{C.}$ to $T^\circ \text{C.}$ It is necessary therefore to measure $R^\circ \text{C.}$, $T^\circ \text{C.}$, N_{0R} , and N_{0T} only, as $\bar{\alpha}$ is known with sufficient accuracy for all the materials investigated.

2. The Method of Excitation.

To measure N_{or} and N_{ot} the bar is forced into transverse vibration by the action of superposed alternating and direct magnetic fields on a small piece of Stalloy—the armature—fixed to its free end. By varying the frequency of the alternating field the amplitude of forced vibration of the bar may be adjusted to its maximum; the frequency at maximum amplitude is the resonant frequency of the bar. The theory of the method has been investigated by Davies and James^{1, 2} who show that, owing to interaction between the armature and the magnetic fields, the frequency N_1 which gives maximum amplitude differs from the natural frequency N_0 of the bar. Consequently they give a method of determining N_0 from N_1 by extrapolating to zero driving and magnetizing fields and infinite air-gap.

Further, damping has an effect on the resonant frequency of the bar. If N_a be the frequency given by the peak of the amplitude-frequency curve at a given temperature, and N_1 the apparent resonant frequency of the bar, then :

$$N_a^2 = N_1^2 (1 - \delta^2/2)$$

in which δ is a function of the damping of the bar, its mass, and frequency N_1 . It was found that, in these experiments, $\delta^2/2$ at room temperature was always less than 0.0001 and so could be neglected. The damping may, however, increase rapidly with temperature so that this assumption may not be true at high temperatures. Resonance curves were therefore taken for all specimens at various temperatures, and in this way it was established that the damping was never sufficient to make N_a appreciably different from N_1 .

The annealed specimens investigated tend to be soft or imperfectly elastic; they do not therefore obey Hooke's law for finite deformations, and hysteresis effects are present. Some of the materials studied, in addition to being imperfectly elastic, are also ferromagnetic at temperatures below their Curie points. The Young's modulus of a ferromagnetic substance, moreover, is a function of the magnetic field in which it is situated. Davies and Thomas¹⁶ give a suitable definition of Young's modulus for imperfectly elastic and ferromagnetic materials of this type, and show that extrapolation to limiting conditions of zero driving and magnetizing fields will give correct values of the modulus. It was found in the present work that, owing to the sensitivity of the method of detecting resonance, there was no appreciable difference between the resonant frequency in the magnetic field and the true resonant frequency.

III.—EXPERIMENTAL ARRANGEMENTS AND METHOD.

1. The Production and Detection of the Vibration of the Bar.

(a) Driving Apparatus.

For convenience and accuracy, the present measurements are best made with bars having resonant frequencies in the acoustic range. Such frequencies are given by bars 2–3 cm. long, about 0.5 cm. wide, and

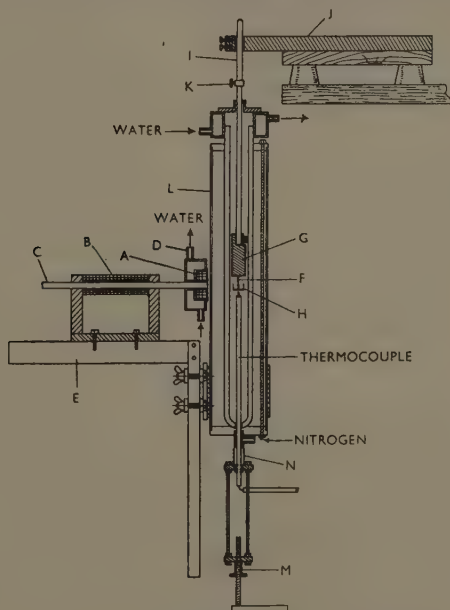


FIG. 1.—General Arrangement of Apparatus.

0.1 cm. thick. The electromagnetic method employed to maintain the bar in forced, transverse vibration may be described by reference to Fig. 1. The alternating-current driving coil *A*, cooled by a water jacket, and the direct-current magnetizing coil *B* are supported by the horizontal cylindrical soft iron core *C*, which may be moved in the direction of its axis and clamped in any desired position. *C* is, in turn, supported by the heavy inverted U-section girder *E* which is bolted to a shelf fitted to the wall. The experimental bar *F*, fitted to the heavy clamp *G*, is excited by the action of the superposed alternating and steady magnetic fields on the Stalloy armature *H*.

The alternating current for the driving coil is generated by a dynatron oscillator, whose frequency is continuously variable in the acoustic range, and its output is amplified by a 45-W. mains-driven amplifier of conventional design.

(b) *Detection of Resonance.*

As the experimental bar has to be surrounded by a furnace, existing methods for detecting resonance were found to be unsuitable. The present method consists in transmitting the vibration of the bar to the needle of an electromagnetic gramophone pick-up. The alternating voltage thus generated in the pick-up is amplified, rectified, and applied to a galvanometer, resonance being indicated by maximum deflection of the galvanometer. The over-all sensitivity of the system is such that an input of $1\text{ }\mu\text{V.}$ at a frequency of 1 kc./s. to the amplifier gives a galvanometer deflection of 2 mm.

The detailed arrangement is shown in Fig. 1. The bar *F* is firmly secured to the brass cylinder *G* by one of the methods described below. *G*, in turn, is attached to the long porcelain rod *I*, which is clamped at the other end in a heavy brass bar *J*. *J* is supported through an anti-vibration rubber mounting on a slate slab fitted to the wall. The vibration is transmitted to the pick-up through a small platform *K* on which the needle rests, the pick-up arm being perpendicular to the section shown in Fig. 1, and attached to the same platform as the bar *J* to further minimize extraneous vibration effects.

The vibrating system just described really consists of two systems coupled together: the bar *F* loaded with the Stalloy armature *H*, and the porcelain rod *I* loaded with the brass cylinder *G*. The combined system thus has two resonant frequencies, one of which is found by the method described above. This resonant frequency may be taken as that of the loaded bar when the natural frequency of the brass cylinder on the porcelain rod is sufficiently low. With the dimensions given in paragraph (a) above, the error introduced by this effect was in every case less than 0.2%. This was checked before every experimental run by determining the resonant frequency of the complete system at room temperature in the present apparatus, and also of the clamped bar itself by observation under a microscope of its maximum amplitude.

(c) *Measurement of Frequency.*

The frequency of the alternating current used to drive the bar is measured by means of the frequency bridge described by one of the authors.¹⁷ The accuracy of the bridge was checked periodically by

comparison with a phonic motor, and the absolute error in frequency was never greater than 0.1%.

(d) *The Clamped, Loaded Bar.*

The bar is attached at one end to the brass cylinder *G* of length 7.5 cm. and dia. 3 cm. As Young's modulus is a function of the fourth power of the vibrating length, it is important that conditions at the fixed end remain unchanged at all temperatures. Bearing this in mind, one or more of the following three methods of providing a fixed end were used satisfactorily:

(i) Both bar and cylinder were milled from a single piece of material. This method can only be used when the specimen is available in sufficient quantity.

(ii) Bar was silver-soldered to the brass cylinder. This method was found to be satisfactory for all specimens subsequently annealed.

(iii) Specimen, in cylindrical form, was screwed tightly into the brass cylinder and then milled into shape.

In each case the Stalloy armature is securely attached to the bar by silver-soldering or riveting.

2. *The Furnace and Measurement of Temperature.*

(a) *The Furnace.*

The specimen is heated in a tubular electric furnace (Fig. 1) in which the heating element is a coil of non-magnetic nickel-chrome wire wound bifilarly on a silica tube with its upper end open and surrounded by a water jacket. The furnace is lagged with kieselguhr packed into an asbestos tube, 4 in. dia. and 20 in. long. It is movable in the direction of its axis to enable the specimen to be correctly positioned.

To avoid oxidation of the specimens at high temperatures, a slow stream of oxygen-free air is passed through the furnace. Further, to prevent the formation of iron nitride at temperatures approaching 500° C., the Stalloy armature, and, when necessary, the specimen, are lightly nickel plated.

(b) *Temperature Measurement.*

The temperature of the specimen is measured with a Chromel/P-Alumel thermocouple, introduced through a hole in the bottom of the furnace. The thermocouple is brought into contact with the specimen only when measuring its temperature, by turning the screw *M* and thus compressing the metallic bellows *N*. The cold junction is enclosed in a water-cooled brass block and its temperature measured with a mercury-in-glass thermometer. The thermocouple was calibrated many times

during the course of the work by the method of calibration at fixed points recommended by the National Physical Laboratory and the U.S. National Bureau of Standards. The fixed points used were the freezing points of pure tin, lead, zinc, and antimony.

It is evident that a temperature gradient may exist along the specimen even when temperature equilibrium has been reached, in spite of the long furnace with concentrated windings at its ends. This gradient was therefore measured under typical experimental conditions for various equilibrium temperatures using a number of thermocouples; in the range 15° – 640° C. the maximum variation over the specimen was found to be less than 2° C., and in the range 15° – 440° C., less than 1° C. This is only so when equilibrium has been attained, i.e. in about 1 hr., for a temperature change of 50° C.

IV.—EXPERIMENTAL RESULTS.

1. *Specimens Investigated.*

These are detailed in Table I. They were all annealed in their final form in a vacuum electric furnace. The pure specimens of copper, nickel, iron, and cobalt were Hilger's "H.S." Brand, the nickel alloys were supplied by Messrs. Henry Wiggin and Co., and the β brass and copper-gold alloy were prepared to specification by Messrs. Johnson, Matthey and Co.

2. *Experimental Curves.*

The results are shown graphically in Figs. 2–6, in which the ratios E_T/E_R (corrected for thermal expansion) are plotted as ordinates and the temperature as abscissa. For each material, two or three specimens cut from the same rod and each, where possible, differently clamped, were investigated under conditions of increasing and decreasing temperature. To illustrate the accuracy and reproducibility of the results, in the curves reproduced for pure nickel and cobalt (Fig. 2), the results for silver-soldered bars are shown as points, those for screwed bars as circles, and those for milled bars as triangles. In each case the points without tails were taken under conditions of increasing temperature, and those with tails under conditions of decreasing temperature.

V.—DISCUSSION OF RESULTS AND METHOD.

1. *Experimental Curves.*

Apart from the intrinsic and technical interest of the results, the curves show three types of discontinuity :

- (a) due to change in the crystal structure of the material (cobalt);
- (b) due to transformations of atomic arrangements within the crystals, that is, from the ordered to the disordered state (CuZn , Cu_3Au);

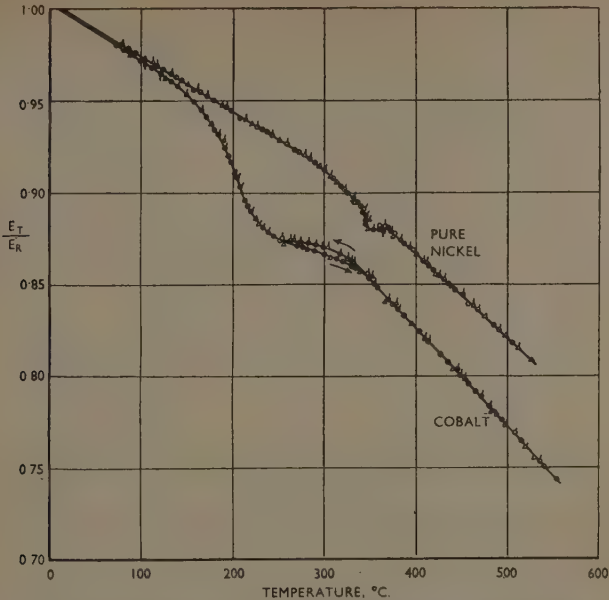


FIG. 2.—Young's Modulus *versus* Temperature Curves for Pure Nickel and Cobalt (tails denote points taken with temperature decreasing).

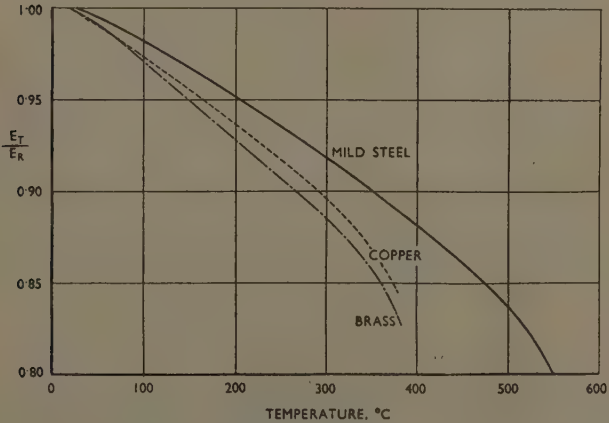


FIG. 3.—Young's Modulus *versus* Temperature Curves for Brass, Mild Steel, and Copper.

(c) at the Curie temperature, at which ferromagnetic substances become paramagnetic (nickel, iron, Monel metal, iron-48% nickel alloy).

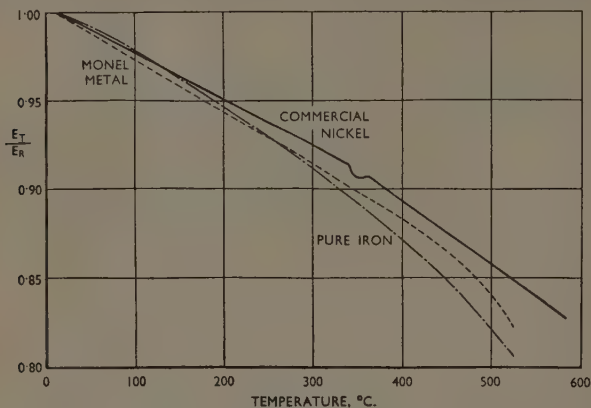


FIG. 4.—Young's Modulus *versus* Temperature Curves for Commercial Nickel, Pure Iron, and Monel Metal.

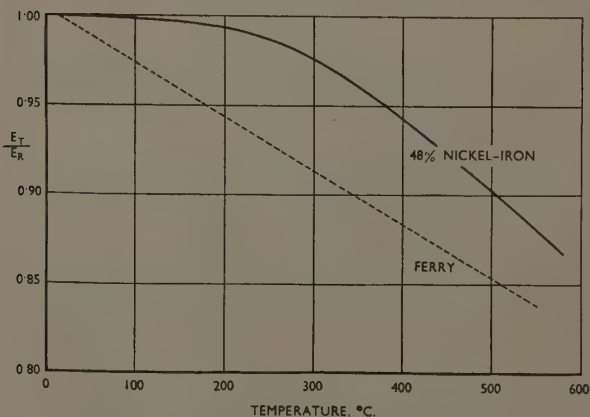


FIG. 5.—Young's Modulus *versus* Temperature Curves for Ferry and Iron-48% Nickel Alloy.

For all the materials investigated in which there is no crystal change or re-arrangement of atoms in the crystal, the variation in Young's modulus as the temperature increases is a linear decrease at first, followed

at higher temperatures by a decrease at a faster rate. This variation is of the same nature as that deduced theoretically by Brillouin¹⁸ for the rigidity modulus. At a critical temperature a discontinuity occurs. The curves taken under conditions of increasing and decreasing temperatures are identical, except in the case of cobalt (Fig. 2) which shows a

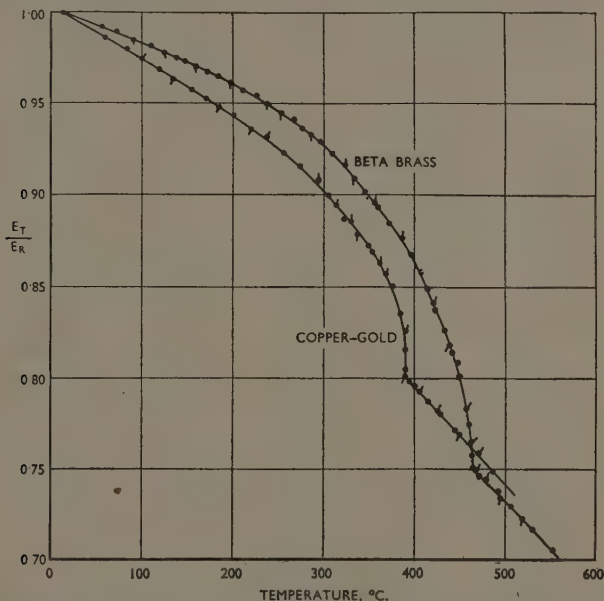


FIG. 6.—Young's Modulus *versus* Temperature Curves for Beta Brass and Copper-Gold Alloy (tails denote points taken with temperature decreasing).

slight difference in the region 250°–350° C. The lack of hysteresis, except for cobalt, is due to the slow rate at which the experimental points are taken, the specimen being given ample time to attain its equilibrium state at the temperature at which each measurement is made. The slight irregularity in the case of cobalt may be explained by the well known fact that this change is one in which equilibrium is attained at a comparatively slow rate.

Discontinuities at Critical Temperatures.

(i) The only substance investigated showing a change in crystal structure was cobalt (Fig. 2), where the change occurs between 450° and 500° C. In the range 250°–350° C., the decrease in Young's modulus

TABLE I.—Details of Specimens.

Material	Composition	Impurities	Heat-Treatment		Curie or Transformation Temperature, °C.	Mean Coeff. of Linear Expansion ($\times 10^6$)
			Temperature, °C.	Time, hr.		
Commercial brass	circa 66% Cu, 34% Zn.	...	700°	6	...	19
Copper	99.98% Cu.	Oxygen, Fe, Ag, As, Bi, Mg, Pb, Sb, Sn.	700°	6	...	18
Commercial nickel	99.2% Ni.	...	650°	29	...	15
Pure nickel	99.97% Ni.	C, Fe, Si.	650°	8	355°	15
Iron	99.75% Fe.	C, Si, Mn, S, Ni, Cr, Mo, V.	700°	6	780°	10
Mild steel	98.83% Fe, 0.25% C, 0.65% Mn.	Si, P, S, Ni, Cr, Mo, V.	700°	6	...	10
Cobalt	99.8% Co.	Ni.	700°	5	{ 450° † } 1110° *	12
Monel metal	67% Ni, 28% Cu.	Fe, Mn.	650°	12	100°	16
Ferry	44% Ni, 56% Cu.	...	650°	9
Iron-48% nickel alloy	48% Ni, 52% Fe.	...	650°	10	425°	10
β brass	48% Zn, 52% Cu.	Fe, S.	670°	16	460°	20
Copper-gold alloy (Cu ₃ Au)	49.2% Cu, 50.8% Au.	...	670°	3	385°	...

* Allotropic change.

† Curie temp.

with increasing temperature is very small, while outside this range it is comparatively large. This peculiarity occurs well below the transition temperature, in agreement with unpublished permeability-temperature curves taken by one of the authors.

(ii) With the exception of iron and cobalt, the ferromagnetic specimens were investigated between room temperature and a temperature beyond their Curie points. In the case of commercial nickel (Fig. 4), the change between 15° and about 330° C., and again between about 360° C. and the highest temperature reached, is linear. The slope above the Curie point is, however, greater. In the range 330° – 370° C. there is a definite irregularity in the curve. This agrees with the established experimental fact that the abnormal change starts below the critical temperature of 355° C. and is complete at a higher temperature. The curve for the pure specimen (Fig. 2) has the same general form except that, in this case, discontinuity in the neighbourhood of 350° C. is preceded by a change of slope at about 300° C.

The curves for the ferromagnetic alloys (Figs. 4 and 5) are quite regular, with no trace of a discontinuity or hysteresis in the neighbourhood of the Curie temperature.

(iii) The curves for the order-disorder alloys, β brass (CuZn), and the copper-gold alloy (Cu₃Au), Fig. 6, agree qualitatively with the theoretical deduction that the degree of order decreases very rapidly as the critical temperature is approached. It is also seen that the equilibrium state of points taken under conditions of temperature increasing and decreasing lies on the same curve.

2. Accuracy.

These curves involve the measurement of temperature and frequency, and are independent of the dimensions of the test specimen. Taking into account the probable errors in the thermocouple calibration and subsequent temperature measurements, any steady temperature can be measured to within 0.2° C. The actual accuracy obtained, however, is determined by the constancy of the temperature of the specimen during the measurement of its natural frequency and the temperature gradient along the specimen. The time required to measure the resonant frequency is so small that the temperature in this period may be regarded as constant. If the bar is left at the equilibrium temperature of the furnace for about an hour, the variation along it is never greater than 2° C. at the highest temperature used. In fact, below about 500° C., this variation was found to be less than 1° C. In addition, the thermocouple is in contact with the bar during all temperature measurements. It may thus be safely deduced that the error in the temperature measurement is

seldom greater than 1°C . (equivalent to a change in Young's modulus of the order of 0.05%).

Frequency is measured with an A.C. bridge with an error of less than 0.1% . There are, however, two other possible errors, one due to inefficient clamping of the bar and the other due to the fact that the vibrating system has two degrees of freedom. Efficient clamping of the bar is established in each investigation by the fact that the resonant frequencies at room temperature before and after a day's run, up to a high

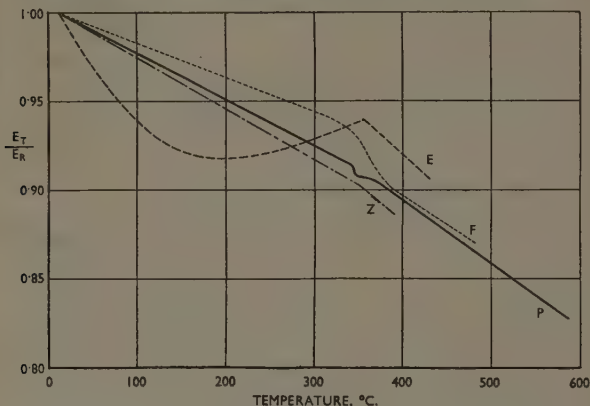


FIG. 7.—Comparison of Young's Modulus *versus* Temperature Curves for Nickel, Obtained by Previous Workers.

E.—Engler (1937).⁸

F.—Förster and Köster (1937).¹⁹

Z.—Zacharias (1933).⁶

P.—Present work (commercial nickel).

temperature and down again, agree to 0.1% . The second source of error is avoided by determining, by visual observation of resonance, the resonant frequency of the bar-cylinder vibrating system at room temperature. This value usually agrees with the combined resonant frequency to better than 0.2% . The absolute error in the measurement of resonant frequency is therefore of the order of 0.2% . As ratios only are required, the relative error in our experimental run is probably less than this.

3. Comparison with the Results of Previous Investigations.

(a) Nickel (Fig. 7).

Experimental results have been given previously by Engler,⁸ Förster and Köster,¹⁹ and Zacharias⁶; they are reproduced in the curves of

Fig. 7. The four curves show dissimilarities which are due in part to differences in the purity and thermal treatments of the specimens. Purity seems to have by far the smaller effect, as the two curves for nickel specimens of different purity, and also for iron, in the present work are in fair agreement. Moreover, Zacharias ⁶ has investigated a number of nickel specimens, all of the same purity but with different thermal histories, and has found that, as the annealing temperature is increased, the curve below the Curie point falls more and more below the straight line *Z* of Fig. 7. He also finds that this part of the curve remains linear until the annealing temperature is 900° C., or greater. Above the Curie temperature, all his curves are linear. These curves also illustrate the well known fact that the temperature of annealing is more significant than the time of annealing.

Siegel and Quimby ⁷ give a curve for nickel of 99.7% purity, annealed at 1100° C. for 4 hr., which agrees with Engler's results.

(b) *Cobalt* (Fig. 8).

Previous results by Engler ⁸ and Förster and Köster ¹⁹ are reproduced in Fig. 8. The arrows in Engler's curve indicate the condition of temperature under which the experimental points were taken, whether increasing or decreasing. There is an appreciable hysteresis in the region of the allotropic transformation. The curve reproduced for Förster and Köster was taken under conditions of temperature increasing; that for temperature decreasing is very different. It is significant in these curves that the value of Young's modulus does not return to its initial value after heating and then cooling to room temperature. This suggests a spurious effect, such as a change in the elastic properties of the specimen due to annealing, or a change in the conditions of the experiment.

(c) *Iron* (Fig. 4).

The present results for iron are in excellent agreement with those of Engler on a specimen of vacuum-smelted electrolytic iron.

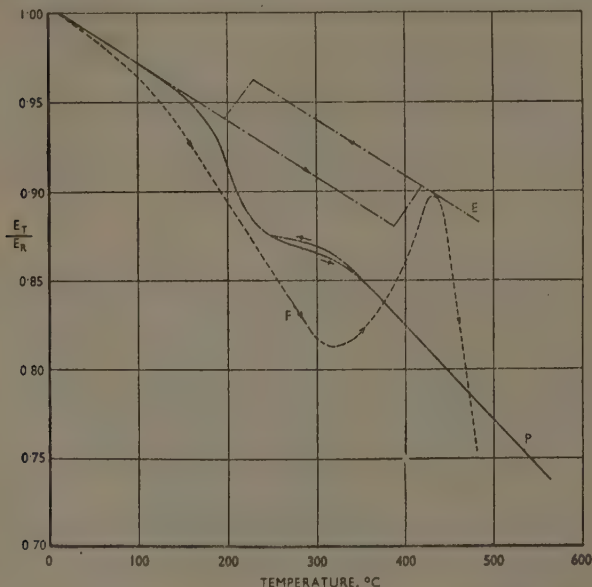
(d) *β brass* (Fig. 6).

The present curve has the same form as that of Förster and Köster, ¹⁹ and both show the same type of discontinuity at the critical temperature. The latter work gives no points taken under conditions of temperature decreasing.

(e) *Nickel Alloys* (Figs. 4 and 5).

The results for Monel metal are in disagreement with those of Nakamura, ²⁰ who investigated eight nickel-copper alloys up to 500° C.

Nakamura found that for alloys with a copper content less than 13 wt.-%, Young's modulus decreases with increasing temperature below the Curie point; at this temperature there is a sharp bend and above it the modulus again decreases with increase in temperature. For alloys with more than 13 wt.-% of copper, on the other hand, Young's modulus increases with increasing temperature, with a sharp bend at the Curie



[FIG. 8.—Comparison of Young's Modulus *versus* Temperature Curves for Cobalt, Obtained by Previous Workers.

E.—Engler (1937).⁸

F.—Förster and Köster (1937).¹⁰

P.—Present work.

point. The present results for Monel metal (28% copper) and also for Ferry (56% copper) show a regular decrease in Young's modulus with increasing temperature with no discontinuity at the Curie point.

The result for the iron-48% nickel alloy is interesting on account of the very small variation of Young's modulus with temperature below about 300° C. This agrees with Guillaume's work²¹ on some nickel-iron alloys, and compares with Waller's result for Elinvar.²²

4. *General Discussion of the Method.*

Since the present method has not been used previously, a brief discussion of its applicability is appropriate. The results obtained establish conclusively the validity of the experimental arrangements. Measurements were made in most cases on three separate specimens of the same metal, all of the same composition and thermal history, but clamped by different methods. The resonant frequencies of the specimens were arbitrarily chosen in the range 500–2000 c./s., and also their dimensions and Stalloy load, consistent with a suitable resonant frequency in this range. The results show that the points taken for each set of specimens are in agreement well within the predicted experimental error.

The sensitivity of the method is of primary importance, as small amplitudes of vibration are the most convenient to generate. More important still is the fact that the amplitude should be kept as small as possible so that the material should obey Hooke's law, even at high temperatures, when it is likely to take a permanent set with ease. The sensitivity is determined by the type of pick-up used, the amplification provided, and the sensitivity of the galvanometer. It could be increased by increasing the sensitivity of any one of these. Unlimited increase, however, is undesirable owing to the effect of extraneous vibrations on the vibrating system and the greater tendency to instability. The results demonstrate that with the present apparatus, the sensitivity is sufficient for any likely determination of the temperature variation of Young's modulus.

Apart from the advantages of ease and convenience over other dynamic methods—the only quantity to measure, apart from temperature, being the frequency of an alternating current—a further definite advantage exists from the point of view of temperature measurements. For accuracy in the determination of the temperature of the specimen, it is desirable that its dimensions be as small as possible to minimize the temperature gradient along it, an effect which might easily introduce a serious error into the temperature measurement. Differences between the present method, in which the specimen is about 2.5 cm. long, and other methods are striking; for example, Engler⁸ used a specimen 50 cm. long, and Förster and Köster¹⁹ one 20 cm. long. Small specimens are also generally more easily obtainable in the pure state, and they lend themselves better to a well defined thermal treatment. These considerations indicate that the method is specially adapted to measurements on small specimens, and might therefore be suitable for investigations on monocrystalline specimens.

ACKNOWLEDGEMENTS.

The authors wish to acknowledge their indebtedness to the late Professor E. J. Williams, F.R.S., for his constant interest and valuable suggestions in the course of the work. One of the authors (G. E. B.) is indebted to the Glamorgan County Council for a Post-Graduate Studentship.

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THE SYSTEM SILVER-MAGNESIUM-TIN, WITH 1182 REFERENCE TO THE THEORY OF TERNARY ALLOYS.*

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WITH AN APPENDIX ON THE STRUCTURE OF THE β' SUPERLATTICE.

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SYNOPSIS.

In connection with the development of the theory of ternary alloys, the system silver-magnesium-tin has been examined by microscopic and X-ray methods. Isothermals have been established at 550° and 450° C.; these show that both the close-packed hexagonal ζ phase of the silver-tin system, and the body-centred cubic β' phase of the silver-magnesium system, have considerable ranges of homogeneity in the ternary diagram. The experiments at 450° C. allow the form of the equilibrium relations over the whole range of compositions to be deduced, and it is found that Mg_2Sn enters into equilibrium with the β' phase, but not with the ζ phase. In the range examined, there are five three-phase triangles, involving the following phases:

- (1) α , β' , and ζ .
- (2) ζ , γ , and β' .
- (3) β' , γ , and Mg_2Sn .
- (4) β' , Mg_2Sn , and Mg_3Ag .
- (5) Mg_3Ag , Mg_2Sn , and Mg .

The β' phase in the silver-magnesium alloys has the caesium chloride structure; the first additions of tin to this structure occur in a random manner, but after a critical tin content has been exceeded, the tin atoms assume ordered positions to produce a superlattice of the Fe_3Al type. This structure is described.

The results are discussed in terms of general alloy theory, and it is shown that, in this system, the electrochemical interaction between the solute atoms is of importance in governing the general form of the equilibria and certain details of the equilibrium diagram. Thus, the primary solid-solubility isothermal is concave towards the silver-rich corner of the diagram, and attains its maximum electron : atom ratio at the point where magnesium and tin atoms are in the ratio 2 : 1. The $\zeta/(\zeta + \beta')$ boundary also occurs at this atomic ratio, and it is suggested that some degree of short-range order exists. The influence of the effective size factor in the ternary system on the ranges of homogeneity of the $3/2$ electron compounds is discussed in detail.

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I.—INTRODUCTION.

THE theory of alloy formation as applied to the binary alloys of copper, silver, and gold with elements of the B-Sub-Groups of the Periodic Table has now reached a relatively satisfactory state, and a large number of alloy systems may be interpreted in terms of three main factors. These factors are connected, respectively, with the number of valency electrons present per atom, the difference in the atomic diameters of the component metals, and the electrochemical characteristics of the components. Detailed discussions of alloy formation from this viewpoint have been published.^{1, 2, 3}

Relatively little consideration, however, has been given to the theory of equilibrium relationships in ternary alloys based on copper, silver, and gold. The effect of various factors on the primary solid-solubility isothermals in ternary alloys has been considered by Hume-Rothery,⁴ and it has been shown that, although the form of the isothermal may differ only slightly from a straight line joining the binary solubility limits in cases where both solutes are of favourable size factor with respect to the solvent, in many cases relatively large deviations from ideal behaviour may occur. The effect of stable compound formation between the two solute elements on the form of the solvent-rich solubility isothermal is particularly striking, and it is of interest to consider the conditions under which the stable compound formed can enter into equilibrium with the primary solid solution. The general form of a ternary isothermal can frequently be interpreted in terms of the relative heats of formation of the phases which occur in the system,⁵ and only intermetallic compounds of the solute elements whose heats of formation are high compared with those of other phases in the system may be expected to enter into equilibrium with the solvent-rich alloys.

In ternary systems based on copper, silver, and gold, the relationships between the 3/2 electron compounds are of particular interest. Binary 3/2 electron compounds may have body-centred cubic, close-packed hexagonal, or β -manganese crystal structures, and the particular structure assumed depends upon the size factor of the solute with respect to the solvent, the solute valency, and the temperature.⁶ If the size factor is defined as $\frac{(d_{\text{solute}} - d_{\text{solvent}}) \times 100}{d_{\text{solvent}}}$, where d is the interatomic distance

in the crystal structure of the element, then the close-packed hexagonal phases tend to occur at low positive or negative values of the size factor. Increasing size factor favours the body-centred cubic structures at the expense of the hexagonal type, while increasing solute valency favours

hexagonal structures. Increasing temperature favours the assumption of the cubic structure.

Similar considerations may be applied to ternary systems ABC , where the solvent A is silver or copper.^{5,7} If, in the binary systems AB and AC , cubic $3/2$ electron compounds are formed, then, at the appropriate temperatures, complete solid solution occurs between the two phases. If, however, one $3/2$ electron compound is cubic and the other hexagonal, their ranges of homogeneity are separated, in the ternary isothermal diagram, by a two-phase region. The limiting compositions to which the hexagonal and cubic structures can persist in the ternary alloys depend on the effective size factor in the ternary system. To a first approximation, this may be expressed, for an alloy containing x at.-% of solute B and y at.-% of solute C , as $\frac{x F_B + y F_C}{x + y}$,

where F_B and F_C are, respectively, the size factors of the solutes B and C with respect to the solvent. Thus, in the system silver-antimony-zinc, the hexagonal silver-antimony $3/2$ electron compound persists from a size factor of $+0.52$ to an effective size factor of -5.75 , which is almost identical with that at which the hexagonal structure begins to give place to the cubic structure in binary silver alloys.⁵

It appears probable, therefore, that the characteristics of ternary alloys based on copper and silver may be to a large extent interpreted in terms of the binary alloys of the same solvent which fall within the same size-factor range. In extension of this work, an experimental examination of the system silver-magnesium-tin has been carried out. This system was selected for investigation for the following reasons:

(1) The binary system silver-magnesium contains a body-centred cubic $3/2$ electron compound β' * which, owing to the relatively high difference in the electrochemical characteristics of silver and magnesium, is ordered from low temperatures to the melting point. The silver-tin system contains a close-packed hexagonal $3/2$ electron compound ζ ,* for which the electrochemical factor is relatively low. The results were thus expected to give information on the relationships between the two structures, the effect of a third metal on the ordered β' phase, the effect of varying the effective size factor, and the influence of "diluting" the high electrochemical factor of the silver-magnesium alloys.

(2) The system magnesium-tin contains the stable compound Mg_2Sn , the equilibrium relationships of which in the ternary system are of interest.

The present paper describes the results of the investigation of the silver-magnesium-tin alloys.

* The nomenclature used is that of Hume-Rothery, Reynolds, and Raynor.⁴

II.—THE BINARY SYSTEMS.

1. The System Silver-Magnesium.

For the purposes of this work the silver-magnesium equilibrium diagram (Fig. 1) is satisfactorily established. The silver-rich region, up to 40 at.-% of magnesium, is taken from the work of Andrews and Hume-

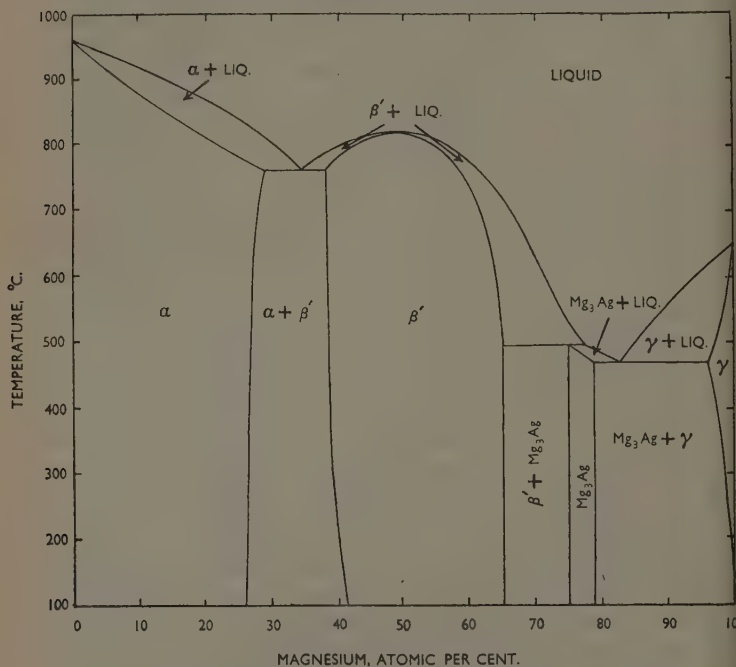


FIG. 1.—The Equilibrium Diagram of the Silver-Magnesium System.

Rothery,⁸ while the remainder of the diagram is based on that given by Hansen,⁹ and incorporates the work of Payne and Haughton¹⁰ and of Hume-Rothery and Butchers²⁴ in the magnesium-rich region. The solid solubility of magnesium in silver is 29.3 at.-% at the eutectic temperature of 759.3° C., and falls to 26.5 at.-% at 300° C. The range of homogeneity of the β' phase (38–65 at.-% magnesium) decreases slightly with falling temperature; the structure of this phase is of the

ordered caesium chloride type at all temperatures. The phase denoted Mg_3Ag is an intermetallic compound of relatively narrow range of homogeneity.

During the course of the present work an account of an X-ray investigation of the system was published by Letner and Sidhu.¹¹ In certain respects their results are inconsistent with Fig. 1; in particular, alloys of composition 29 and 42 at.-% magnesium, annealed at 525°C ., are stated to be respectively homogeneous α and $(\alpha + \beta')$ in constitution. In order to check these results, alloys of the same compositions have been annealed for 7 days at 550°C .; after treatment they consisted respectively of the $(\alpha + \beta')$ and β' phases. The results given by Andrews and Hume-Rothery are therefore preferred.

2. The System Silver-Tin.

The equilibrium diagram of the silver-tin system is shown in Fig. 2, which is constructed from the results of Murphy,¹² Hume-Rothery,

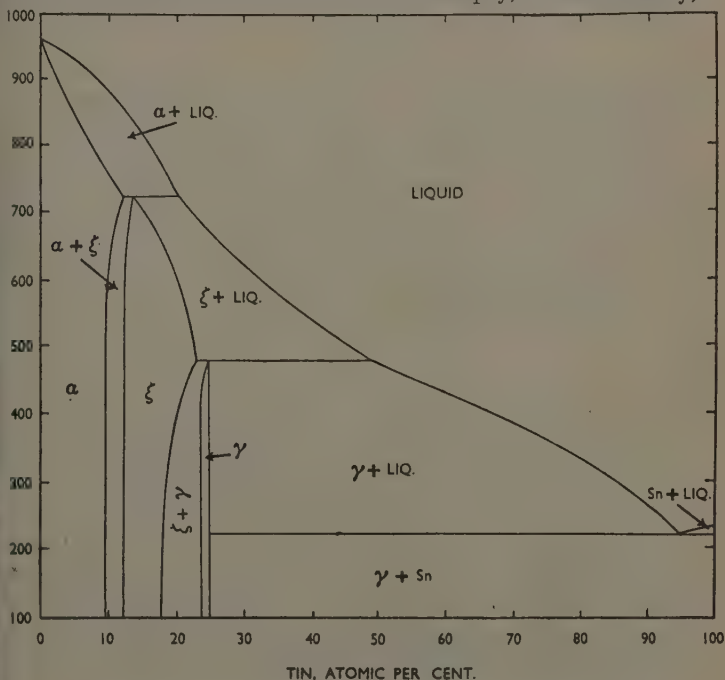


FIG. 2.—The Equilibrium Diagram of the Silver-Tin System.

Mabbott, and Channel-Evans,¹³ and Owen and Roberts.¹⁴ The maximum solid solubility of tin in silver is 12.2 at.-% at 724° C., and decreases to 9.7 at.-% at 300° C. The ζ phase, which is a 3/2 electron compound, extends from 12.3 to 22.7 at.-% of tin, but the upper limit decreases to 18.0 at.-% of tin at 200° C. The crystal structure of this phase is close-packed hexagonal,¹⁵ while that of the phase denoted Ag_3Sn (γ) is a deformed modification of the hexagonal structure.

3. The System Magnesium-Tin.

Fig. 3 shows the equilibrium diagram for the magnesium-tin alloys. The most important feature in relation to the present work is the

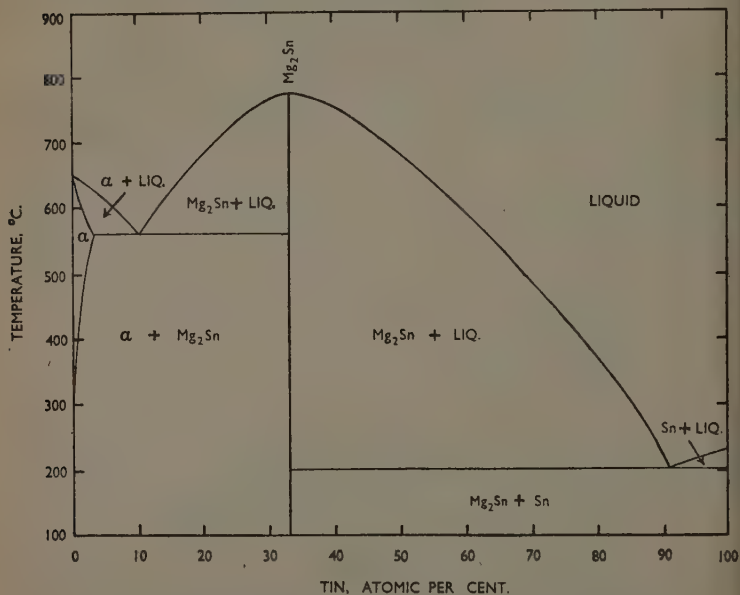


FIG. 3.—The Equilibrium Diagram of the Magnesium-Tin System.

presence of the intermetallic compound Mg_2Sn , which is anti-isomorphous with fluorspar, CaF_2 .¹⁶

No reference to any previous work on the ternary system silver-magnesium-tin was found in the literature.

III.—MATERIALS USED.

In the examination of the system, some 90 ternary alloys were prepared. The following materials were used throughout :

(1) Assay silver, 99.99% pure, supplied by Messrs. Johnson, Matthey and Co. Ltd.

(2) Magnesium, 99.95% pure, supplied by Messrs. F. A. Hughes and Co. Ltd.

(3) Chempur tin, 99.992% pure, obtained from Messrs. Capper Pass and Son Ltd.

All alloys prepared were therefore of the same high degree of purity.

IV.—GENERAL EXPERIMENTAL METHODS.

The experimental methods used were closely similar to those described in previous publications.¹⁷

1. *Melting and Casting.*

Alloys were prepared, in quantities of 10 g., by melting together the appropriate amounts of silver and tin in Salamander crucibles, and adding the magnesium in relatively large pieces to avoid excessive loss by oxidation and volatilization. For silver-rich alloys, potassium chloride was used as a flux, but for the lower-melting alloys a flux based on anhydrous magnesium chloride was more convenient. In some cases, in which it was desirable to prepare alloys with an accurately predetermined composition, portions of previously analysed ternary alloys were melted together. After thorough stirring, the molten alloys were cast into cold copper moulds.

2. *Annealing Treatments.*

For annealing, sections of the ingots were enclosed in evacuated glass capsules and heated in tubular resistance furnaces controlled to within $\pm 0.5^\circ$ C. of the required temperatures by Foster regulators. Chill-cast alloys were heated slowly to the annealing temperature to absorb low-melting constituents. In general, an annealing time of 7 days was used at temperatures above 500° C.; below this temperature, at least 10 days were given. Specimens from all treatments were quenched in cold water.

Annealing temperatures were measured with a periodically calibrated platinum/platinum-rhodium thermocouple, used in conjunction with an accurate potentiometer.

3. Micrography of the Alloys.

For metallographic examination, new surfaces of all specimens were exposed by a saw cut, and prepared in the usual manner. The final polish was applied with "Silvo" on a Selvyt pad.

No ternary compounds were observed in the course of the work, and the binary phases encountered were those already discussed. These phases could be distinguished with certainty in whatever combinations they occurred. The most generally useful etching reagent was a solution of 20 g. of chromium trioxide and 1.5 g. of sodium sulphate in 100 c.c. of water. Alloys were etched by immersion for approximately 5 sec.; the optimum time depended on the nature of the constituents present. Using this reagent, the α and β' phases appeared yellow and brown, respectively. Homogeneous ζ alloys remained white, but appeared pale blue in the presence of α or β' . In three-phase ($\alpha + \beta' + \zeta$) alloys, the appearances of the α and ζ phases were somewhat similar, but contrast between these phases was improved by following the chromic acid treatment by a 1 sec. immersion in ammonia and hydrogen peroxide, after which the α appeared light brown.

A 5% potassium dichromate solution was more convenient for alloys rich in tin and magnesium. With this reagent, Ag_3Sn appeared brown while the ζ phase with which it was usually associated remained white.

Alloys containing Mg_3Ag and Mg_2Sn were best examined in the unetched state, owing to the highly reactive nature of these phases. Both appeared dark in the microstructures, owing to deterioration of the surface during preparation; distinction between them was based mainly on the observation that Mg_3Ag occurred as discrete particles, while Mg_2Sn usually appeared in an orientated type of structure. X-ray examination (see below) confirmed this distinction. Typical microstructures are shown in Figs. 4, 5, 6, and 7 (Plate CII).

4. X-Ray Methods.

The X-ray Debye-Scherrer technique was employed throughout to confirm the micrographic results and to indicate the crystal structures of the phases observed. In addition, the changes which occur when tin replaces some of the magnesium in the ordered silver-magnesium β' phase were studied.

Filings were prepared from the annealed ingots, and re-annealed *in vacuo*, for the relief of strain, at the temperature from which the ingots had been quenched. After annealing, specimens were rapidly cooled in an air blast. Control experiments during the early stages of the work showed that the results obtained were not affected by the quench-

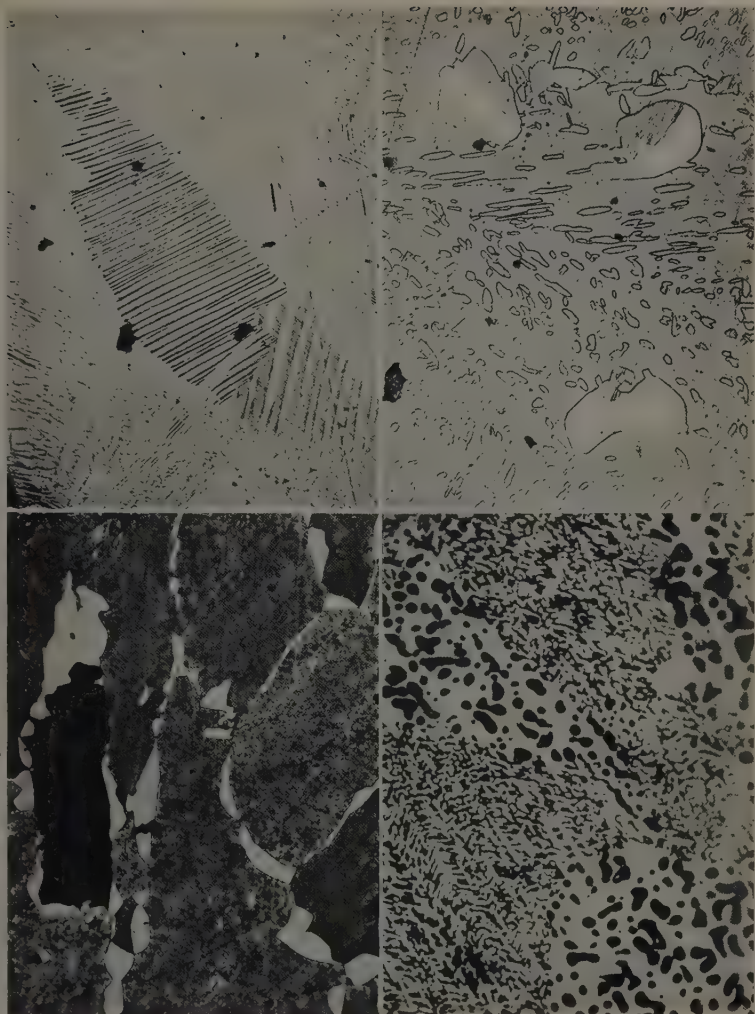


FIG. 4.—Alloy 27·13/7·97 Annealed at 550° C. β' + precipitate of ζ . $\times 150$.
 FIG. 5.—Alloy 27·13/7·97 Annealed at 450° C. β' + precipitate of ζ and α . α is the darker of the precipitated constituents. $\times 150$.
 FIG. 6.—Alloy 25·71/6·56 Annealed at 550° C. β' matrix, α precipitate inside grains and at boundaries. $\times 150$.
 FIG. 7.—Alloy 49·38/12·67 Annealed at 450° C. β' matrix, globular Mg_3Ag and angular Mg_2Sn . $\times 150$.

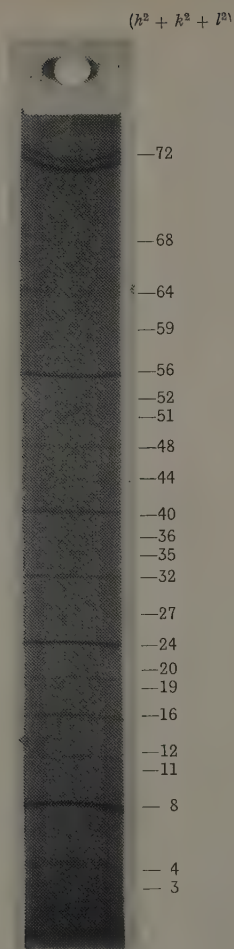


FIG. 8.—Diffraction Pattern of Alloy 33.0/7.0.

ing rate. The annealed filings were mounted on a glass fibre with Canada balsam, and exposed to copper $K\alpha$ radiation in a 9-cm. cylindrical camera. Specimens were not sieved, owing to the risk of materially altering the proportions of different phases present in the process. The resulting diffraction patterns were compared with standard patterns obtained by exposing pure specimens of the binary phases which occur in the ternary system.

5. Analytical Control.

Owing to the volatility of magnesium and the risk of loss by oxidation during melting, the actual micrographically examined specimens of all critical alloys were analysed. Since the totals of the percentages of the three components for several alloys were satisfactory, the general procedure was to determine either the tin and magnesium, or the tin and silver percentages.

6. Nomenclature.

In order to facilitate reference to individual alloys, specimens are referred to in terms of the atomic percentages of magnesium and tin. Thus, the term "alloy 7.0/15.0" denotes an alloy with 7 at.-% of magnesium and 15 at.-% of tin.

V.—EXPERIMENTAL RESULTS.

The results obtained may be most conveniently described by considering the isothermal sections established, and the X-ray experiments in support of them.

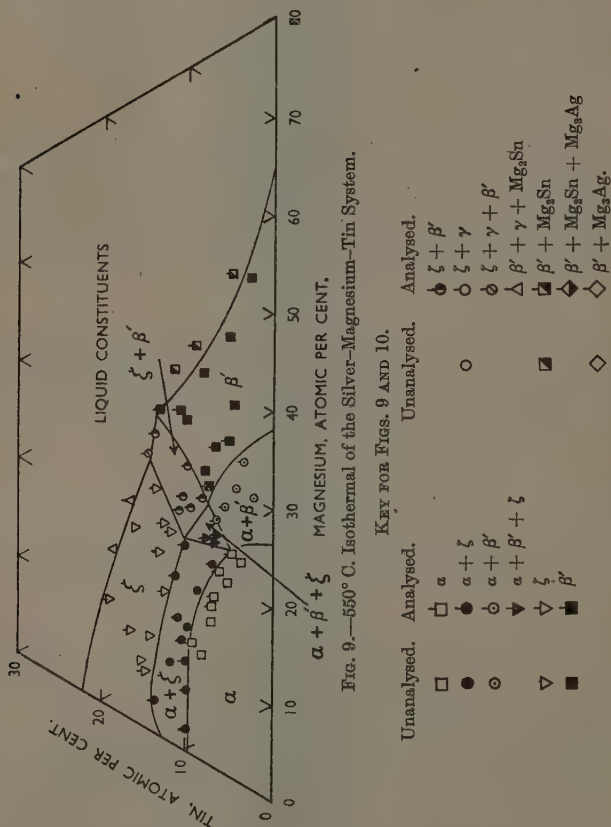
1. The Isothermal at 550° C.

The results of the annealing treatments at 550° C. are summarized in Fig. 9; analysed alloys have been distinguished by the addition to the appropriate symbol of a small bar.

Fig. 9 shows that the primary solid-solubility isothermal is not a straight line joining the binary solubility limits, which are satisfactorily fixed by previous work on the binary systems. The ternary solid solubility is greater than in the ideal case. The $\alpha/(\alpha + \zeta)$ boundary is accurately located by the points plotted, while the short $\alpha/(\alpha + \beta')$ boundary is fixed by the binary limit and the homogeneous alloy 23.19/4.68. The latter alloy lies very close to the point at which the three-phase ($\alpha + \beta' + \zeta$) triangle touches the primary solid solubility isothermal.

The $(\alpha + \zeta)/\zeta$ boundary is located by the brackets shown in Fig. 9;

the ($\alpha + \zeta$) two-phase region widens slightly as the magnesium content increases. The other boundaries call for little comment, but it should be noted that the three-phase triangle ($\alpha + \beta' + \zeta$) is accurately fixed



by the three alloys which contain three phases, by the ($\alpha + \zeta$) alloy 21.1/10.1, by the ($\alpha + \beta'$) alloy 25.71/6.56, and by the ($\beta' + \zeta$) alloys 24.23/9.65 and 27.13/7.97.

At 550° C., both the ζ and β' phases are in equilibrium with liquid along their solute-rich boundaries, so that the equilibrium relations in

the solid state are completely defined. The equilibrium between the two $3/2$ electron compounds is simple, and a narrow two-phase region intervenes between the two homogeneous phase fields. The α phase enters into equilibrium with both electron compounds, and the solubility isothermal is markedly concave towards the silver-rich corner of the diagram. Neither the solubility of tin, nor that of magnesium, is markedly altered by the presence of the third element.

2. The Isothermal at 450° C.

The results at 450° C. were established by annealing both chill-cast alloys and alloys previously annealed at 550° C. Several extra alloys were prepared, and the silver-rich region was again examined in detail. Though only a few alloys rich in tin and magnesium were investigated, the results enabled the form of the equilibria for the whole range of compositions to be determined. The isothermal is shown in Fig. 10.

In the silver-rich region, only two alloys showed a change in structure from that at 550° C. Alloy 6.84/9.69 ($(\alpha + \zeta)$ at 550° C.) consisted entirely of the α phase at 450° C., while alloy 27.13/7.97 ($(\beta' + \zeta)$ at 550° C.) became three-phase ($\alpha + \beta' + \zeta$) at 450° C. The effect of these changes on the form of the isothermal is slight. The boundary between the β' and $(\beta' + \zeta)$ fields is moved slightly towards the silver-magnesium axis; this is confirmed by the presence, in the $(\beta' + \zeta)$ alloy 29.76/9.77, of somewhat more of the ζ phase than at 550° C.

The equilibrium relationships on the solute-rich side of the β' and ζ regions are complex, and of interest. The fields containing Mg_3Ag were relatively easily distinguished owing to the characteristic globular structure observed. Alloy 42.0/9.0 contained only a trace of Mg_3Ag , and lies close to the phase boundary. In the adjoining $(\beta' + \text{Mg}_3\text{Ag} + \text{Mg}_2\text{Sn})$ field, Mg_2Sn was difficult to detect micrographically, but after identification of this field by X-rays (see below) it was possible to develop a distinction between Mg_3Ag and Mg_2Sn on the basis of the form of their occurrence. In general, Mg_2Sn does not appear in the typical globular form of Mg_3Ag (see Fig. 7, Plate CII). Three $(\beta' + \text{Mg}_3\text{Ag} + \text{Mg}_2\text{Sn})$ alloys were obtained, which, together with other results, enabled the sides of the three-phase triangle to be approximately located. For this purpose, it may be assumed that the solubility of silver in Mg_2Sn is limited; the form of the homogeneous Mg_3Ag field is not accurately known, but must project into the ternary model sufficiently far to allow alloy 67.5/5.0 to contain only the β' and Mg_3Ag phases. The existence of the $(\beta' + \text{Mg}_3\text{Ag} + \text{Mg}_2\text{Sn})$ field implies equilibrium between Mg_3Ag and Mg_2Sn , so that the phase fields in the magnesium-rich region may also be drawn.

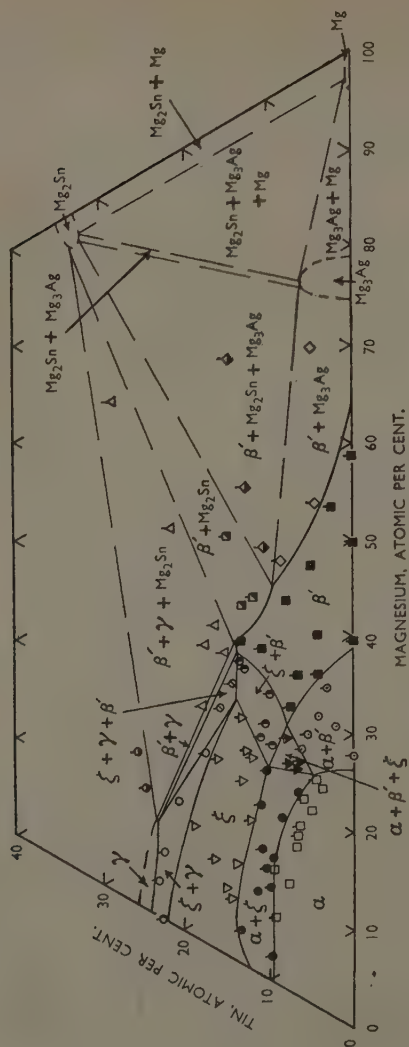
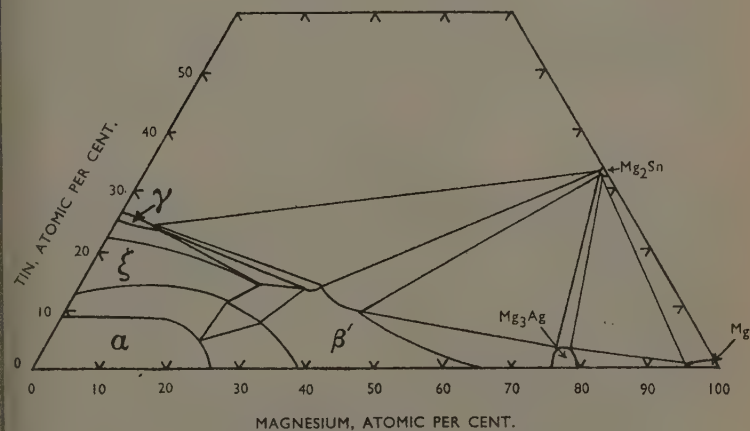
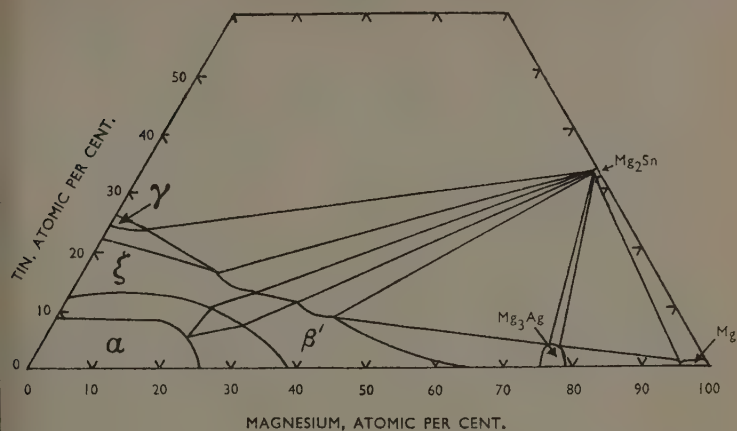


FIG. 10.—450° C. Isothermal of the Silver-Magnesium-Tin System. (For key see Fig. 9).

Once equilibrium between β' and Mg_2Sn is established, there are two possible ways in which the remainder of the phase fields may be distributed,



FIGS. 11 and 12.—Possible Forms of the Ternary Equilibrium Relations Involving Mg_2Sn and the γ Phase.

buted, as shown in Figs. 11 and 12. Equilibrium between ζ and Mg_2Sn would involve a large ($\zeta + \gamma + \text{Mg}_2\text{Sn}$) field (Fig. 11); if, however, the γ and β' phases enter into equilibrium, the ($\zeta + \text{Mg}_2\text{Sn}$) equilibrium is prevented, and a large ($\beta' + \gamma + \text{Mg}_2\text{Sn}$) field results (Fig. 12). No

microstructures or diffraction patterns corresponding to Fig. 11 were observed, but (Fig. 10) six alloys were found to lie in a ($\beta' + \gamma + \text{Mg}_2\text{Sn}$) field. Two alloys contained the β' , γ , and ζ phases. The existence of these two three-phase triangles implies a ($\beta' + \gamma$) field, which must, however, be narrow, as indicated by the two ($\beta' + \zeta$) alloys 30.47/13.08 and 30.93/13.5. Although no alloy examined contained only the β' and γ phases, the position of this field must be very close to that given in Fig. 10. The other phase boundaries are adequately fixed by the structures of alloys lying in adjacent fields, and no other arrangement is consistent with the experimental results.

The form of the $\beta' / (\beta' + \text{Mg}_2\text{Sn})$ boundary is of interest. The point at which it touches the ($\beta' + \gamma + \text{Mg}_2\text{Sn}$) triangle is located by the three three-phase alloys 33.83/16.53, 31.0/15.0, and 30.79/17.71, and by the homogeneous β alloy 33.23/13.54. The point at which the boundary touches the apex of the ($\beta' + \text{Mg}_2\text{Sn} + \text{Mg}_3\text{Ag}$) triangle must be close to the ($\beta' + \text{Mg}_3\text{Ag}$) alloy 42.0/9.0. The $\beta' / (\beta' + \text{Mg}_2\text{Sn})$ boundary cannot therefore be a smooth continuation of the $\beta' / (\beta' + \text{Mg}_3\text{Ag})$ boundary. This is consistent with the thermodynamical requirement¹⁸ that the two boundaries of the single-phase field, when produced, must either both lie in the three-phase triangle, or one on each side of it. The boundary in Fig. 10 is drawn in its most probable position, with a distinct change in direction at the apex of the ($\beta' + \text{Mg}_2\text{Sn} + \text{Mg}_3\text{Ag}$) triangle. Further reference will be made to this below (Section VII).

3. X-Ray Experiments.

The X-ray experiments were of much assistance in elucidating the complex equilibria described above. The filings irradiated were taken from the actual micro-specimens examined, and the diffraction patterns were compared with those obtained from the β' , ζ , α , γ , Mg_3Ag , and Mg_2Sn phases. Some twenty-five polyphase alloys were examined. In addition, twenty homogeneous β' alloys were investigated; the results of this work are described in Section VI.

The existence of the ($\beta' + \text{Mg}_3\text{Ag} + \text{Mg}_2\text{Sn}$) field was confirmed by the diffraction patterns of the three alloys lying in this field at 450° C. Similarly, the structures of all the six alloys lying in the ($\beta' + \gamma + \text{Mg}_2\text{Sn}$) triangle were confirmed by their diffraction patterns. Of the four alloys lying within the three-phase ($\alpha + \beta' + \zeta$) triangle at 550° C., alloys 23.47/6.66 and 24.43/6.23 gave patterns in which the contributions from all three phases were clearly visible; alloys 27.13/7.97 and 23.38/7.56 showed a face-centred cubic diffraction pattern on which was superimposed, respectively, a body-centred cubic and a close-packed

hexagonal pattern. All four alloys, however, contained the same three phases, according to the micrographic examination. The various two-phase fields were also adequately confirmed by the diffraction patterns obtained, as in Table I.

TABLE I.

Phase field	Number of alloys examined
($\alpha + \zeta$)	8
($\gamma + \zeta$)	4
($\beta' + \text{Mg}_2\text{Sn}$)	2
($\beta' + \text{Mg}_3\text{Ag}$)	1
($\alpha + \beta'$)	4

A number of supplementary experiments involving partially molten alloys was also carried out, with results in accordance with the equilibria summarized in Figs. 9 and 10.

4. General Summary.

At 550° C., the ζ and β' phases have considerable ranges of homogeneity, and are separated by a relatively narrow two-phase region. The solute-rich boundaries of these phases involve equilibrium with the liquid at this temperature. The primary solid solubility isothermal is markedly concave towards the origin. The form of this curve is more fully discussed below (Section VII).

At 450° C., the form of the equilibria in the silver-rich region is similar to that at 550° C. A slight increase in the primary solid solubility occurs, and the $\beta'/(\beta' + \zeta)$ boundary moves slightly towards the silver-magnesium axis. Both Mg_2Sn and the γ phase of the silver-tin system enter into equilibrium with the β' phase, and the form of the phase fields at the higher percentages of magnesium and tin is governed by these equilibria.

VI.—THE STRUCTURE OF THE TERNARY β' PHASE.

The crystal structure of the β' phase in the binary silver-magnesium system is of the caesium chloride type, in which one type of atom occurs at the body centres, and another type at the cube corners, of the cubic unit cell. Several specimens of the ternary β' phase were submitted to X-ray analysis, and the initial results showed that in some cases extra lines, which could not be accounted for on the basis of a simple caesium chloride structure, were present in the diffraction patterns. These extra lines were placed close to the superlattice lines, and were of similar

intensity (Fig. 8, Plate CIII). It was noted that while alloy 38.4/4.25 gave a diffraction pattern corresponding to the caesium chloride structure, alloy 33.0/6.77 gave a pattern containing the extra lines. A systematic examination of the alloys lying within the β' field was therefore undertaken.

Fig. 13 summarizes the homogeneous β' alloys examined; all alloys lying below the broken line possessed the caesium chloride structure, while those lying above the line gave diffraction patterns containing extra lines. A special alloy 33.0/7.0, the diffraction pattern of which is shown in Fig. 8, was selected for further study. Separate powder specimens were respectively quenched, air-cooled, and furnace-cooled from 550° C., but no change in the pattern was observed. High-temperature experiments with this alloy showed that, on heating the

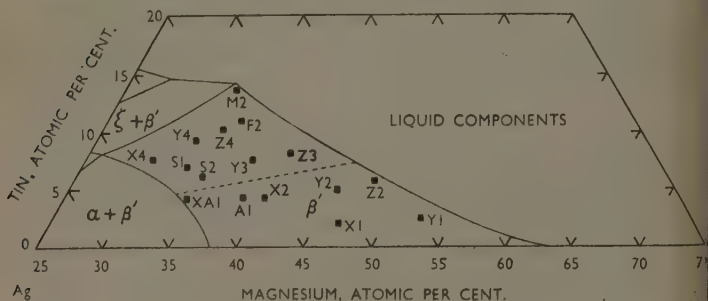


FIG. 13.—Alloys in the β' Field which were Examined by the X-Ray Method.

specimen, the extra reflections disappeared at approximately 450° C., while the normal superlattice lines disappeared at approximately 650° C. Above this temperature, only reflections due to a disordered body-centred cubic structure were observed. This strongly suggests that the extra reflections are due to an ordering of the tin atoms in the already ordered silver-magnesium phase, which takes place sufficiently rapidly on cooling to be incapable of suppression by quenching. It is also of interest that the binary β' phase remains ordered up to its melting point (820° C.), whereas the addition of 7.0 at.-% of tin depresses the normal order \rightleftharpoons disorder transformation to approximately 650° C.

All the diffraction lines on films of the type of Fig. 8 could be indexed on the basis of a unit cell of side equal to double that of the unit cell of the parent caesium chloride structure. The lines observed are consistent with the reflections from a structure with face-centred cubic symmetry, except that the (533) and (733) reflections were apparently missing from

certain films. Intensity calculations, which were carried out by the authors' colleague Mr. W. H. Hall, subsequently showed that the theoretical intensities of these two lines were very low, which is consistent with their non-recognition on the film.

The details of the intensity calculations have been kindly summarized by Mr. Hall in an Appendix to this paper (p. 805), and show that the structure of the ternary β' phase containing more tin than corresponds to the broken line in Fig. 13 may be regarded as four interpenetrating face-centred cubic lattices, which combine to form a body-centred cubic pattern of half their spacing. The ternary ordered β' structure is thus similar to that of Fe_3Al , and is shown in Fig. 14. For the actual alloys, the positions of the silver and magnesium atoms are as given in Fig. 14, and the sites characterized by open circles in this Figure are occupied by tin, silver, and magnesium atoms together. Thus, in the alloy considered, (33.0/7.0), eight silver atoms occupy the sites assigned to silver in Fig. 14, and four magnesium atoms occupy the magnesium positions. The remaining four positions are filled by tin, silver, and magnesium atoms in the ratio 1:12 : 1:60 : 1:28.

When tin, therefore, is introduced into the ordered silver-magnesium β' phase, it at first replaces the other atoms in a random manner. After a critical concentration has been reached, the tin atoms begin to segregate into definite positions in the structure in such a manner as to keep as far as possible from the large magnesium atoms present.

During the course of the work, the lattice spacings of the alloys 46.5/2.0, 40.0/4.0, 34.5/6.0, and 30.0/7.5, which traverse the β' field, were measured. The observed spacings were corrected for experimental errors by the extrapolation method of Nelson and Riley,¹⁹ and were calculated as the side of the small body-centred unit cube for both the caesium chloride and more complex structures. Fig. 15 shows the results obtained; between 4 and 6 at.-% of tin, a marked increase in the rate of contraction occurs. Throughout this series, the magnesium content decreases; since, however, the work of Letner and Sidhu¹¹ indicates that the lattice spacing of the β' phase varies linearly with

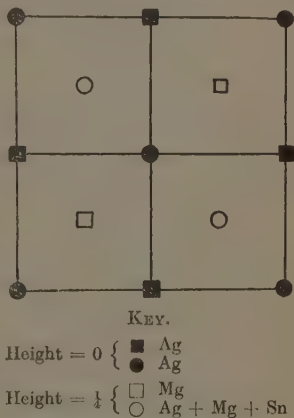


FIG. 14.—Unit Cell of the Tin-Rich β' Phase.

composition, it is improbable that the decreasing magnesium content is responsible for the relatively sudden contraction observed. This

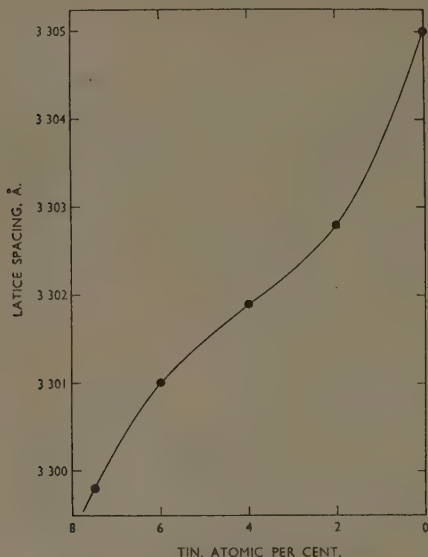


FIG. 15.—Lattice Spacings of β' Alloys.

contraction is therefore associated with the onset of the ordering of the tin atoms.

Equilibrium between the two $3/2$ electron compounds therefore involves the close-packed hexagonal ζ phase and a cubic β' phase which is as fully ordered with respect to all three components as its composition allows.

VII.—DISCUSSION OF THE RESULTS.

Several points of interest arise in connection with the forms of the isothermal diagrams. These may be considered in turn.

1. *The General Form of the Equilibrium Relations.*

Figs. 9 and 10 show that the binary compound Mg_2Sn does not enter into equilibrium with the primary solid solution; in the system copper-magnesium-tin, however, equilibrium between Mg_2Sn and the copper-rich alloys is observed. This may be interpreted in terms of the free

energies of the phases concerned. It has been suggested⁵ that, as a first approximation, the heats of formation of intermetallic phases may be taken as a measure of the relative free energies. Unfortunately, only the heat of formation of Mg_2Sn (5.6 kg.cal./g. atom) is known. For the other phases of the system under consideration, however, heats of mixing in the liquid state are available, and are collected in Table II.

TABLE II.

Phase Heat of mixing, kg. cal./g. atom	$\text{MgAg} (\beta')$ 3.0	Mg_3Ag 2.5	Ag_3Sn 1.2	$\text{Ag}_6\text{Sn} (\zeta)$ 0.9
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Heats of formation cannot be derived from heats of mixing without detailed knowledge of latent heats and specific heats of the phases and their components; no accurate development is therefore possible. The heat of mixing of Mg_2Sn , however, is approximately 2 kg.cal./g. atom lower than the heat of formation; similar differences exist for other phases for which both heats of formation and of mixing are known. The heats of formation of the phases listed in Table II are therefore probably of the order of 2 kg.cal./g. atom higher than the values given. From these considerations, and from the form of the equilibrium relations observed, the probable form of the ternary free-energy model may be drawn as in Fig. 16; in this Figure free energy has been drawn as increasing in the downward direction, for ease of drawing. The tangent planes which are common to three free-energy peaks define the three-phase equilibria, and it will be noted that the envelope of the model contains no re-entrant portions, and is everywhere convex in the direction of decreasing free energy.

In the copper-magnesium-tin system, no $3/2$ electron compound is present along the copper-magnesium axis. The phases Cu_2Mg and CuMg_2 occur, but both owe their existence to special size relationships between the large magnesium and the small copper atoms. Consequently, and also because copper is more electropositive than silver, the heats of formation would be expected to be considerably smaller than in the silver-magnesium system. If the heights of the free-energy peaks which occur near to the front face of the free-energy model are reduced, then the arrangement of tangent planes shown in Fig. 16 no longer remains appropriate, since re-entrant portions are developed. Alloys occurring in a wide composition range could attain lower free-energy values by existing as a mixture of the α and Mg_2Sn phases with a third phase, and this factor is responsible for the equilibrium relations in the copper-magnesium-tin alloys. In the silver-magnesium-tin alloys, the

presence of a phase of high heat of formation on the silver-magnesium axis prevents equilibrium between α and Mg_2Sn , whereas the relatively lower heats of formation of the phases in the copper-magnesium system allow this equilibrium to occur.

2. The Primary Solid Solubility.

It has been suggested by Hume-Rothery⁴ that if, in a given ternary system, one solute has a larger atomic diameter than the solvent, while

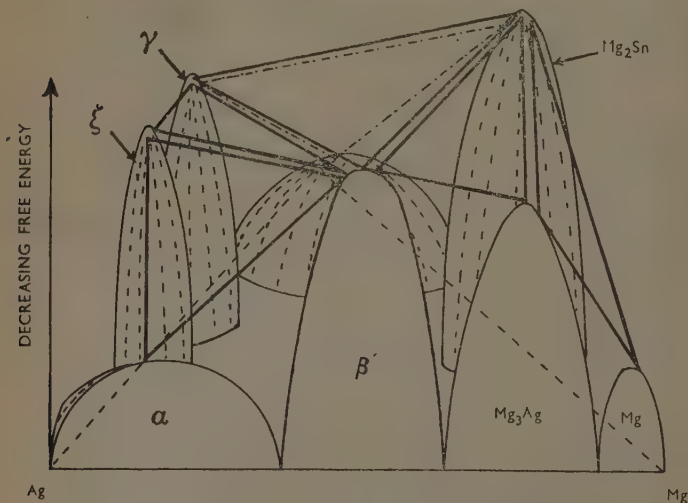


FIG. 16.—The Probable Form of the Ternary Free-Energy Surfaces.

the other solute has a smaller atomic diameter, then, owing to mutual relief of lattice distortion, the area occupied by the primary solid solution is increased relatively to that which would be expected in the ideal case. For the system under discussion, the interatomic distances in the crystals of the elements are as follows :

Magnesium	Silver	Tin
3.190 Å	2.883 Å	2.797 Å

The atomic diameter of the solvent is intermediate between those of the solutes, and, as shown in Figs. 9 and 10, the primary solution area is of the required form; the solubility extends to higher solute percentages than would correspond to a straight line joining the two binary limits.

Assessment of the precise nature of the distortion produced by the

mutual solution of metals of different valencies is, however, difficult. Thus, the solution of tin in silver increases the lattice spacing even though the interatomic distance in tin is smaller than that in silver; it is necessary to recognize that the mean lattice distortion is composed of a factor due to atomic-size differences⁴ and a factor due to valency differences. Increasing solute valency leads to increased expansion, so that, for silver-tin alloys, the two factors oppose. For silver-magnesium alloys the two factors reinforce, but, since magnesium is only divalent, the part of the expansion due to solute valency is less than in the case of tin. It is clear, however, that there is an expansion of the lattice for both systems, so that in each case the distortion at the binary solubility limit is positive. The above-stated interpretation of the form of the isothermal, based on atomic-size considerations only, is thus too superficial, and it is suggested that at least three factors must be considered.

In the first place, at the binary solubility limits the silver lattice is considerably expanded; in the region of centres of local disturbance it may therefore be easier to insert a large atom than in the case of the pure solvent. This would account for the fact that magnesium may be added to the saturated solid solution of tin in silver without seriously affecting the solubility of tin.

Secondly, the local distortions which are of importance from the point of view of solid solution formation may be regarded as composed of both atomic and valency factors, the latter being predominant for the silver-tin system. The introduction of magnesium in place of tin atoms will both reduce the magnitude of the atomic part of the distortion, since the size of the atom is larger than that of the silver atom whereas the tin atom is smaller, and the magnitude of the valency part, by reason of its lower valency. Since the relatively high electrochemical difference between silver and magnesium also tends to give rise to local relative contractions of the interatomic distances in the neighbourhood of a magnesium atom, it is probable that the resultant local disturbance will be much less serious. It is known that the mean distortion produced per atom in silver by magnesium is less than that produced by tin. The total strain to be accommodated by the lattice will thus decrease, giving opportunity for the introduction of further centres of disturbance.

The third factor is connected with the tendency towards compound formation by the two solutes. At 550° C. the electron:atom ratio along the primary solid solubility isothermal rises from 1.3, corresponding to the binary silver-tin alloys, to 1.4, which is very close to the theoretical maximum calculated by Jones,²⁰ and then falls to the value

of 1.26 which corresponds to the silver-magnesium alloys. The rise in electron : atom ratio again suggests that relief of local lattice distortions is occurring, and it is most significant that the maximum occurs very close to the composition at which magnesium and tin atoms are present in the proportions corresponding to Mg_2Sn . This suggests that the electrochemical interaction between the electropositive magnesium and the electronegative tin tends to relieve, by local decreases in the interatomic distances, the positive distortions produced by the tin and magnesium atoms individually, possibly with the formation of some degree of short-range order.

The form of the solid-solubility isothermals may therefore be interpreted in terms of three reinforcing factors :

- (i) The relatively easier insertion of a large atom into an already expanded structure.
- (ii) The relief of distortion due to valency of the solute by a solute of lower valency.
- (iii) The relief of positive distortions by electrochemical interaction between the solutes.

The maximum solid solubility in the ternary system at 550°C . is 28 at.-% of total solute. This occurs at the point at which both ζ and β' are in equilibrium with the primary solid solution, and depends on the relationship between these phases.

3. *The 3/2 Electron Compounds.*

The equilibrium between the β' and ζ phases is simple, and the projection of the area corresponding to each into the body of the ternary diagram is considerable. The ζ phase dissolves 26 at.-% of magnesium, and at this limit the tin content is only 13.5 at.-%. The phase can thus contain nearly twice as many magnesium atoms as tin atoms, while still remaining close-packed hexagonal in structure. The β' phase retains its body-centred cubic structure up to a maximum tin content of 13.5 at.-%.

The two main factors which affect the stabilities of 3/2 electron compounds are the electron : atom ratio and the size factor, to which further reference is made below. It is of interest to examine the variation of electron : atom ratio along the phase boundaries of the β' and ζ phases. In Fig. 17 the solute-rich boundaries have been plotted as $\log [\text{Mg}]$ against $\log [\text{Sn}]$, where $[\text{Mg}]$ and $[\text{Sn}]$ denote atomic percentages of the two solutes. Curves of constant electron : atom ratios 1.65 and 1.70 have also been plotted as broken lines. The $\beta' / (\beta' + \text{Mg}_3\text{Ag})$ boundary AB follows the curve for an electron : atom ratio of 1.65

closely over most of its length, while the $\zeta/(\zeta + \gamma)$ boundary ED follows the curve for the value 1.70. The tendency for the ternary phase-boundaries of an electron compound to occur at a constant electron : atom ratio

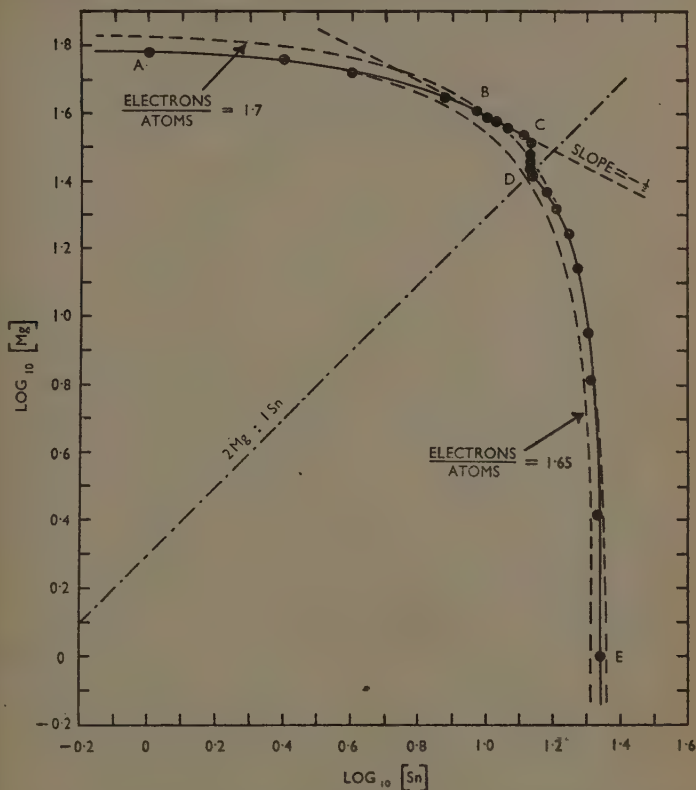


FIG. 17.—Log [Mg] Plotted Against Log [Sn] for the Solute-Rich Boundaries of the β' and ζ Phases at 450° C.

is clearly illustrated. Where the β' phase enters into equilibrium with Mg_2Sn , (BC), the constant electron : atom ratio of 1.65 is no longer obtained; instead, the curve is consistent with the existence of a short straight portion of slope $-\frac{1}{2}$ (Fig. 17). This is the form of logarithmic relation to be expected if this portion of the boundary is governed by the relationship $[\text{Mg}]^2[\text{Sn}] = \text{constant}$. This type of relationship applies to

the primary solid-solubility isothermals of many ternary systems where the solid solution is in equilibrium with an intermetallic compound of substantially fixed composition,^{4, 5} while it is known that the $\epsilon/(\epsilon + \text{ZnSb})$ boundary of the system silver-antimony-zinc, where the $3/2$ electron compound ϵ is in equilibrium with the compound ZnSb, can

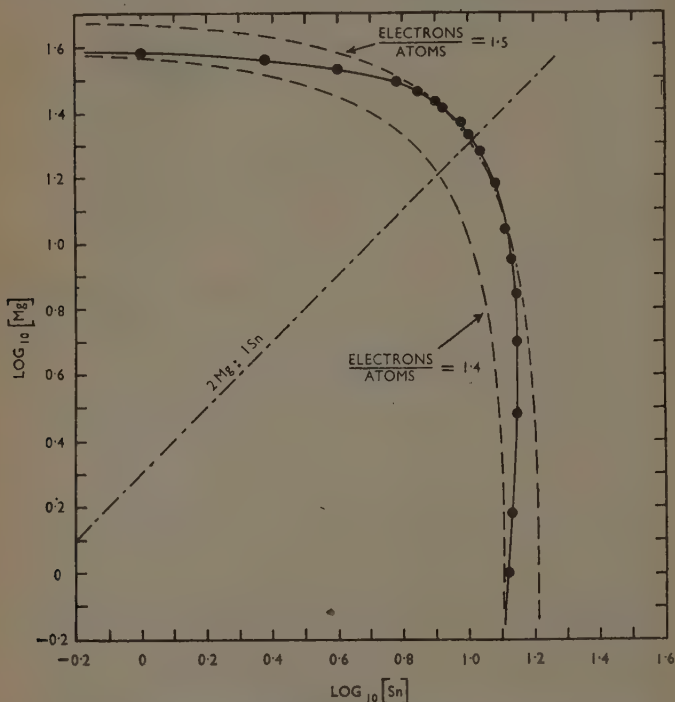


FIG. 18.—Log [Mg] Plotted Against Log [Sn] for the Silver-Rich Boundaries of the β' and ζ Phases at 450° C.

also be represented by the equation $[\text{Zn}][\text{Sb}] = \text{constant}$.⁵ Equilibrium between $3/2$ electron compounds and intermetallic compounds of the electrochemical type is thus controlled by “mass-action” principles in the same way as for primary solid solutions.

Fig. 18 shows a graph of $\log [\text{Mg}]$ against $\log [\text{Sn}]$ for the silver-rich boundaries of the electron compounds. The electron : atom ratio rises rapidly from 1.36 for the silver-tin ζ phase to 1.44 as magnesium replaces

tin up to the point at which the effective size factor (see below) is zero. It then rises more slowly to a maximum of 1.5. The $\beta' / (\beta' + \alpha)$ boundary similarly represents a rise in the electron : atom ratio from 1.38 for the binary alloys to 1.5, which is reached where the β' and ζ phases enter into mutual equilibrium.

In Figs. 17 and 18, lines have been drawn to represent a constant proportion of magnesium to tin atoms of 2 : 1. In each case the maximum electron : atom ratios are reached near to the composition at which the solute atoms are present in the proportions required to form Mg_2Sn . Further, the points along both the silver-rich and solute-rich boundaries at which ζ becomes unstable with respect to β' , correspond to a ratio of two magnesium atoms to one tin atom; as may be seen from Fig. 10, the $\zeta / (\zeta + \beta')$ boundary is a straight line along which the ratio 2Mg : 1Sn is maintained. The fact that the ζ phase is stable up to this particular atomic ratio, and will not take up further magnesium atoms, strongly suggests that there exists among the solute atoms some form of order, probably short-range order since no extra lines were detected in the diffraction patterns of ternary alloys. The structure containing solute atoms in the correct proportions may be regarded as able to distribute the distortion, caused by the presence of the solute atoms, by a relatively orderly arrangement, but is unable to accommodate large magnesium atoms in excess of the 2Mg : 1Sn ratio.

Comparison of Figs. 17 and 18 shows that, as the third element is added to either of the electron compounds, the mean electron : atom ratio rises to a value of approximately 1.6. The ranges of homogeneity from the silver-rich to the solute-rich boundaries of the two ternary phases, when expressed in terms of the electron : atom ratio, do not vary greatly. Thus, the ζ range changes from 0.29 to 0.21 electrons per atom, while the β' range changes from 0.26 to 0.24 electrons per atom, on the addition of the third element.

4. *Influence of the Size Factor on the Ranges of Homogeneity of the 3/2 Electron Compounds.*

In the Introduction to this paper, it has been mentioned that, to a first approximation, the ranges of homogeneity of ternary 3/2 electron compounds may be considered in terms of the effective size factor in the ternary system. The effective size factor for an alloy containing x at.-% of solute B and y at.-% of solute C may be defined as $\frac{x F_B + y F_C}{x + y}$, where F_B and F_C are respectively the size factors for the solutes B and C with respect to the solvent. In the system silver-antimony-zinc at 400° C., according to this conception, the hexagonal silver-antimony

phase extends from an effective size factor of $+0.52$ to one of -5.7 , while the body-centred cubic silver-zinc phase extends from an effective size factor of -7.7 to one of -7.0 . The hexagonal phase is therefore stable down to approximately the same size factor as that at which the hexagonal structures in binary $3/2$ electron compounds with silver are stable; thus, the $3/2$ electron compounds in the systems silver-antimony ($F = +0.52$) and silver-tin ($F = -2.98$) are hexagonal, but in the silver-aluminium system ($F = -5.65$) the hexagonal phase gives place at moderate temperatures to the body-centred cubic phase.

It is of interest to examine the present system from the same point of view. The data summarized by Hume-Rothery, Reynolds, and Raynor⁶ show that, in silver alloys, the $3/2$ electron compounds at temperatures of the order of 500°C . have the structures given in Table III.

TABLE III.

Alloy System	Size Factor	Structure of $3/2$ Electron Compound
AgZn . . .	-7.77	Body-centred cubic
AgAl . . .	-5.65	Close-packed hexagonal
AgSn . . .	-2.98	Close-packed hexagonal
AgSb . . .	$+0.52$	Close-packed hexagonal
AgCd . . .	$+3.12$	Close-packed hexagonal (body-centred cubic at higher temperatures)
AgIn . . .	$+4.75$	
AgMg . . .	$+10.65$	Body-centred cubic

From the fact that the $3/2$ electron compound in the gold-indium system ($F = +4.93$) is also close-packed hexagonal, it may be concluded that this structure may exist over a range of size factors, distributed almost symmetrically on either side of zero, from approximately -6 to $+5$. Outside these limits, the body-centred cubic structure becomes more probable. At higher temperatures, the tendency is for cubic phases to form at the expense of the hexagonal phases; the data suggest, however, that cubic phases do not occur at any temperature between size factors of approximately -4.5 and $+3.0$.

At 550° and 450°C ., the hexagonal ζ phase of the silver-tin system extends in the ternary system from the silver-tin axis ($F = -2.98$) to an effective size factor of $+6.6$ at the silver-rich end, and of $+5.84$ at the solute-rich end, of the $\zeta/(\zeta + \beta')$ boundary. The ternary hexagonal phase thus becomes unstable with respect to the cubic phase at an effective size factor of approximately $+6$, in good qualitative agreement with the value at which the same change occurs in the binary systems. The slightly greater extension of the phase than would be

expected by strict comparison with the binary systems is due to the stabilizing effect caused by the electrochemical interaction between the solute atoms discussed above.

The body-centred cubic β' phase extends from a size factor of $+10.65$ on the silver-magnesium axis to an effective size factor of $+7.77$ at the silver-rich end, and of $+7.0$ at the solute-rich end, of the $\beta' / (\beta' + \zeta)$ boundary. As the temperature is lowered, the $\beta' / (\beta' + \zeta)$ boundary moves slightly towards the silver-magnesium axis, in agreement with the conclusion from a study of binary alloys⁶ that the body-centred cubic structure tends to become less probable with decrease in temperature. In binary systems, a high solute valency favours hexagonal $3/2$ electron compounds at the expense of the cubic structures. For the system studied, the high valency of tin favours the hexagonal structure, while the lower valency of magnesium tends to cause a breakdown of this structure. This effect reinforces the influence of the size factor.

Further general confirmation of the principle that, in ternary systems, the ranges of homogeneity of the $3/2$ electron compounds occupy approximately the same size-factor ranges as in the corresponding binary systems is given by the results of recent work on the copper-aluminium-silicon system.²¹ In binary copper alloys, hexagonal phases occur from size factors of -8 to -4 , and, by analogy with silver and gold alloys, would be expected to persist at zero size factor, though no alloy of copper with a B-Sub-Group metal actually possesses a size factor between -4.15 (copper-germanium) and $+4.23$ (copper-zinc). The body-centred cubic structure persists from size factors of $+9.64$ down to at least $+4.23$. In the copper-aluminium-silicon alloys, therefore, the close-packed hexagonal copper-silicon $3/2$ electron compound would be expected to persist across the diagram to at least an effective size factor of zero, while the cubic copper-aluminium β phase would be expected to persist down to an effective size factor of at least $+4$. The published equilibrium diagram shows that at 650°C ., the hexagonal phase exists between effective size factors of -8 and $+2$, while the cubic phase exists between effective size factors of $+6.6$ and $+3.2$. In this system, the area occupied by the cubic phase decreases as the temperature is lowered, in agreement with the general principles derived from a study of binary alloys.

It is suggested, therefore, that a qualitative guide to the extent to which a ternary $3/2$ electron compound will project into the body of a ternary isothermal diagram may be obtained by a consideration of the effective size factor in the ternary system, in conjunction with a study of the relationship between structure and size factor in the relevant binary alloys.

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where the four interpenetrating face-centred cubic lattices are denoted 1, 2, 3, and 4.

The structure factors for this structure are known (Bradley and Jay²²). Let f_1, f_2 , &c., be the average atomic scattering factors for the

TABLE IV.

Indices of Reflections			$h^2 + k^2 + l^2$	Bragg Angle, degrees	F_{hkl}	Relative Intensities	
Body-centred Cubic Lattice	AgMg Compound	β' Super-lattice				Calculated	Observed
110		111	3	11.8	21.9	8.64	1
		100	4	13.5	39.2	15.67	3
		110	8	19.6	108.3	106.0	>14
		311	11	22.8	18.5	4.26	2
200	200	111	12	23.8	33.4	4.37	2
		400	16	28.0	94.1	18.10	6
		331	19	30.4	16.6	1.85	1
211	210	420	20	31.4	30.0	5.62	2
		211	24	34.9	84.0	35.56	10
		333, 511	27	37.4	15.2	1.37	1
220	220	440	32	41.3	77.1	11.13	4
		531	35	43.6	14.3	1.44	1
		300, 221	36	44.4	26.0	2.90	1.5
310	310	620	40	47.5	72.1	17.10	5
		533	43	...	13.6	0.61	< 0.5
		311	44	50.7	24.8	2.02	1
222	222	444	48	53.8	68.1	5.27	3
		711, 551	51	56.1	13.1	1.23	1
		320	52	57.1	23.8	2.07	1
321	321	642	56	60.6	65.0	34.48	16
		731, 553	59	63.6	12.6	2.19	1.5
400	400	800	64	68.7	62.0	5.59	3
		733	67	...	12.1	1.18	1
		410, 322	68	73.8	22.3	7.93	5
411, 330	411, 330	820, 644	72	81.5	59.5	85.0	18

atoms in positions 1, 2, &c. (Fig. 19). Then the structure factor F_{hkl} for any reflection hkl may have one of three values:

Case 1. Indices all even, sum = $4n$, where n is an integer including zero. These are the main body-centred cubic lattice lines, for which $F_{hkl} = 4(f_1 + f_2 + f_3 + f_4)$.

Case 2. Indices all even, sum $\neq 4n$. These are the AgMg super-lattice lines, for which $F_{hkl} = 4(f_1 + f_2 - f_3 - f_4)$.

Case 3. Indices all odd. These are the extra superlattice lines, for which $F_{hkl} = 4(f_3 - f_4)$.

Thus the intensity of the extra superlattice lines depends on the differential scattering powers associated with the atoms on sites 3 and 4,

and the extra lines only appear when the distribution of atoms between these sites is different. The structure factors can be calculated for any postulated distribution of silver, magnesium, and tin atoms between the four sites. Since in the binary alloys the electrochemical attraction between silver and magnesium results in the formation of a superlattice of considerable stability, it seems likely that in the ternary alloys the structure would be as little different from this superlattice as possible.

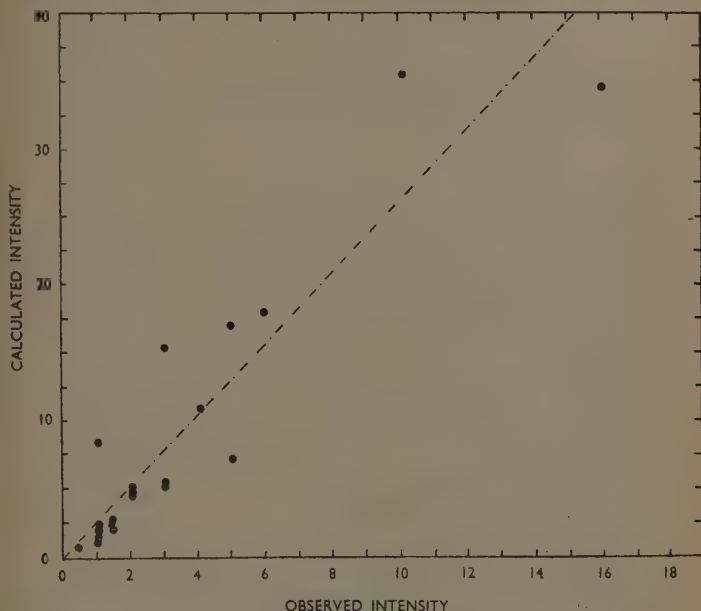


FIG. 20.—Observed and Calculated Intensities for Alloy 33.0/7.0.

Most of the alloys showing the extra superlattice lines contained rather more than the 50% silver present in the binary compound AgMg. The structure shown in Fig. 14 may then be suggested as a possible one; in this structure, the distribution of atoms on three of the component face-centred cubic lattices is exactly the same as in the AgMg superlattice, while all extra silver and tin atoms are accommodated on the fourth face-centred cubic lattice.

The structure-factor terms F_{hkl} have been evaluated on this basis for a typical alloy 33/7, and are listed in Table IV. After squaring and

correcting for multiplicity and trigonometrical factors, theoretical intensities which may be compared with those observed are obtained. No attempt was made to photometer the films accurately, but the intensities of the lines were compared directly with a step wedge such as is used for calibrating films. After correction for background the relative intensities listed in Table IV were obtained. The comparison between observed and calculated intensities is presented in Fig. 20. The statistical correlation coefficient between these values is approximately 0.8; in view of the approximate nature of the estimation of intensity, this degree of agreement is regarded as satisfactory. Similar calculations have been carried out for a number of other possible atomic distributions, but in no case has such significant agreement with experiment been obtained.

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SEGREGATION IN ALUMINIUM-COPPER ALLOYS.*

1183

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(Communication from the British Non-Ferrous Metals Research Association.)

SYNOPSIS.

Segregation was measured in a number of ingots of aluminium-copper alloys containing 3 and 7% copper, solidified in such a way that turbulence was avoided and solidification took place in one direction only. Different rates of cooling were employed. Some of the melts were degassed, some were grain refined, and some were solidified *in vacuo*. Most of the ingots were chilled from the bottom, but the effect of chilling from the top was also investigated.

Three well defined zones were observed in these ingots: (1) An exuded layer of aluminium-copper eutectic at the outer surface of the chilled face. (2) A zone adjacent to the chilled face slightly enriched in copper; this zone was narrower with more rapid cooling. (3) A wider zone at the remote end of the ingot, impoverished in copper and porous. This inverse segregation is accounted for by a theory based on interdendritic flow of residual liquid to compensate for freezing shrinkage, and a quantitative agreement is demonstrated. A few tests with bismuth-6% tin alloy, which expands on solidification, showed the reversal of the segregation effects. From the results of tests it is concluded that capillary forces are the most important factor influencing interdendritic flow in the feeding of solidification shrinkage. Atmospheric pressure, gravitation, and released gases are less important under these conditions of fairly rapid unidirectional solidification.

Additional experiments were made with sand castings cooled from all sides, and with very slowly solidified ingots. Methods of minimizing segregation are outlined.

I.—INTRODUCTION.

THE work now described formed part of a programme of research on segregation which was carried out in the laboratories of the British Non-Ferrous Metals Research Association between 1936 and 1940. As a preliminary to the research, the literature relating to inverse segregation was studied and a review published.¹ An account of the experimental work was issued as a confidential report in 1940, and but for the intervention of the recent war it would have been published earlier. Although several years have elapsed the work is still of fundamental interest, particularly in view of recent developments in continuous casting.

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In the main part of the work quiescent melts were solidified in such a way that solidification took place in one direction, and the segregation was examined. The interdendritic-flow theory of inverse segregation, which is based on the progressive compensation of solidification contraction by residual liquid, was elaborated and found adequate to explain the results. Shortly after the manuscript for the confidential report was prepared in 1940, Brenner and Roth² published a paper in which the same theory was developed along essentially similar lines, and in more recent times it has received general acceptance. For example, Brick³ gave it as the explanation of inverse segregation at the American Institute of Mining and Metallurgical Engineers' Symposium on Segregation in 1944, and Northcott⁴ found it adequate to account for the results of his experimental work on directionally solidified castings.

Other results reported here throw light on the relative importance of factors determining the movement of residual liquid through the interdendritic channels, on the conditions under which normal or inverse segregation may be expected to occur, and on ways of minimizing inverse segregation.

II.—MATERIALS USED.

Aluminium of 99.997% purity and cathode copper of 99.99% purity were used in the preparation of the aluminium-copper alloys. For the experiment with a tin-bismuth alloy the materials used were bismuth of 99.95% purity and Chempur tin of 99.985% purity.

III.—ALUMINIUM-COPPER ALLOYS SOLIDIFIED UNIDIRECTIONALLY.

1. *Experimental Work.*

(a) *Casting Procedure.*

Eight ingots of aluminium-7% copper and four of aluminium-3% copper alloy were cast in the apparatus described below. Details of methods of treating the melts and rates of cooling are set out in Table I. Ingots described in the Table as being of low gas content were treated by the B.N.F. degassing process, i.e. bubbling dry nitrogen through the melt for several minutes, using a flux consisting of 1 part NaF and 2 parts NaCl. Those described as gassy were treated by bubbling a stream of nitrogen saturated with water vapour (at 45° C.) through the melt for 15-20 min.; the rate of flow was about 30 l./hr. Two ingots were treated with a grain-refining flux containing titanium. One ingot was solidified *in vacuo*.

The mould used in this section of the work was shaped like a truncated cone, with a 2-in.-dia. base, and the walls tapered so that an ingot

TABLE I.—Aluminium-Copper Alloy Ingots Solidified Unidirectionally from the Base.

B.N.F. Mark	Average Compos- ition (Nominal), Copper, %	Freezing Range, ° C.	Conditions of Cooling	Gas Content of Melt	Mean Voids, %	See Section III. 2. (d) for Definitions				Thickness of Side Exudation and Extent from Chill Face
						Exudation on Chill Face	Estimated Effect of Exudation on 1st Slice, Copper, %	General "Segrega- tion," Copper, %	"Positive" Segrega- tion, Copper, %	
GNH 1	7	91°	Fast; in air	Low	0.45	Thin	0.2	1.5	0.4	Thick; 2 in.
GNH 2	7	91°	Slow; in air	Low	1.05	Very thin	0.2	1.5	0.5	Very thin; intermittent
GNH 11	7	91°	Intermediate; in air	Low	0.63	Very thick	2.3	1.65	0.5	Moderate; 2 in.
GNH 9	7	91°	Fast; in air	High	1.62	Thick	0.7	1.7	0.35	Thick; 1½ in.
GNH 8	7	91°	Slow; in air	High	1.83	Very thick	3.0	1.9	0.35	Nil
GNH 27	7	100°	Fast; in air;	Low	0.16	Very thin	0.15	0.9	0.5	Thick; 2 in.
		approx.	grain refined							
GNH 28	7	100°	Slow; in air;	Low	0.75	Very thin	0.1	1.1	0.6	Nil
		approx.	grain refined							
GNH 38	7	91°	Fast; in <i>vacuo</i>	Low	0.35	Moderate	0.4	0.8 max.	0.3 max.	Moderate; 1½ in.
GNH 13	3	50°	Fast; in air	Low	0.56	Thin	0.15	0.6	0.15	Moderate; 2 in.
GNH 14	3	50°	Slow; in air	Low	0.89	Thin	0.2	0.75	0.3	Nil
GNH 17	3	50°	Fast; in air	High	0.48	Thin	0.15	0.3	0.2	Moderate; 2 in.
GNH 16	3	50°	Slow; in air	High	0.83	Very thin	0.15	0.9	0.3	Nil

3 in. high had a dia. of about $1\frac{1}{2}$ in. at the top. The general arrangement is illustrated in Figs. 1-3. The object of this design was to minimize any tendency of the ingot to hang up in the mould and thus draw away from the base plate. A steel plate formed the base of the mould, and the wall was of electrode carbon. Four exploring thermocouples were arranged

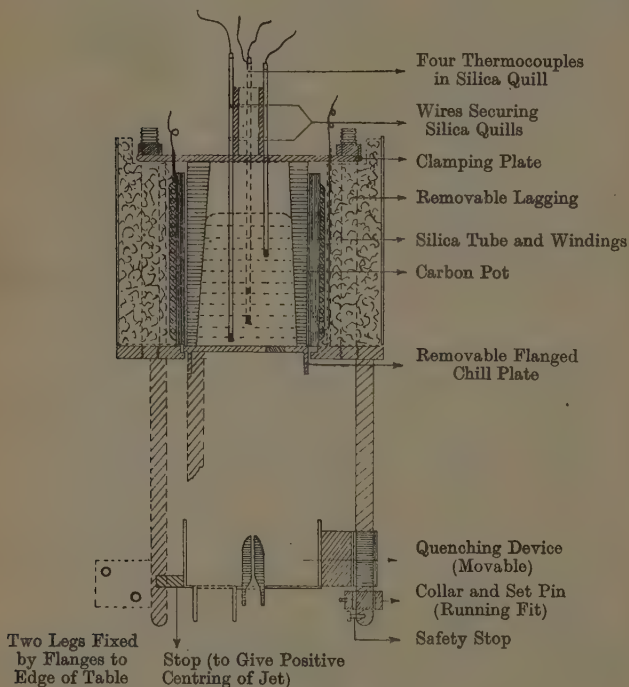


FIG. 1.—Ingot Mould. $\times \frac{1}{4}$.

on a cylindrical surface concentric with the centre of the mould, at distances 0.125, 0.50, 1.25, and 2.00 in. from the chill face.

A similar arrangement was used for alloys cast in a vacuum, except that the whole was built into a silica tube which could be evacuated to a final pressure of 0.01-0.001 mm. of mercury, and the heating was carried out by means of an H.F. induction coil.

To bring about unidirectional solidification the mould was pre-heated, and after introducing the melt the base plate was chilled from

below, rapid chilling being obtained by means of a jet of water flowing at a controlled rate, and slow cooling by a stream of nitrogen, also flowing at a uniform and reproducible rate.

As each ingot cooled, the temperatures registered by the four thermo-

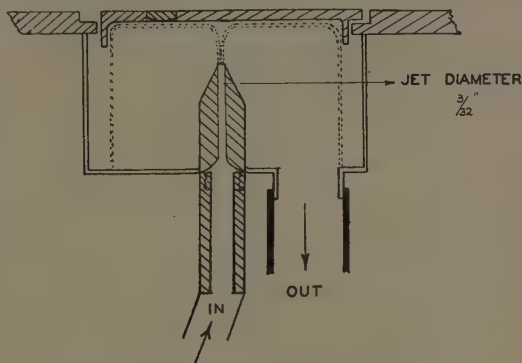


FIG. 2.—Quenching Device in Position. $\times \frac{1}{2}$.

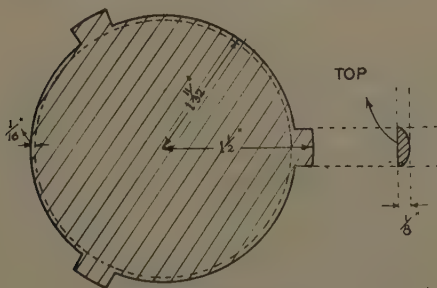


FIG. 3.—Removable Base Plate. $\times \frac{1}{2}$.

couples were recorded with an accuracy of $\pm 0.5^\circ \text{C}$. From the time-temperature data thermal gradient curves were constructed for various times after the beginning of cooling; and from these curves isothermals were drawn to show the extent of the solid, liquid, and intermediate (pasty) regions in the ingot at any given time.

(b) Examination of Ingots.

Macrostructure and microstructure were examined by taking a slice down the whole length of the ingot, just outside the embedded thermocouple wires.

For the measurement of segregation a block about 0.5 in. square in section was cut from between the thermocouples, running from the base to the top of the ingot. The density of this block was measured with an accuracy of the order of 1 part in 1000, and the block was then cut into slices, parallel to the base of the ingot, for detailed measurement of segregation. The region nearest the chill face was the subject of the most careful examination, and here the first four slices were made 0.050 in. thick. The fifth slice was 0.10 in. thick, and in general the remainder was cut up into slices 0.25 in. thick. The density of each slice was measured, and chemical analyses were carried out both on the slices and on the swarf produced by the 0.03-in.-thick cutter used to part off the slices.

Earlier unpublished work on alloys cold worked by various amounts had shown that up to 9% copper the maximum densities of aluminium-copper alloys were represented by a straight line drawn through the points 2.694 g./c.c. at pure aluminium and 2.874 g./c.c. at aluminium-9% copper. From this and the density measurements it was a simple matter to calculate the percentage of voids in each of the slices and to draw a curve showing the variation in porosity with distance from the chill face.

2. Experimental Results.

(a) *Cooling Curves and Isothermals.*

Most of the cooling curves are not in themselves of any great interest. The only noteworthy feature is illustrated in Fig. 4 which shows that for one ingot, chilled at intermediate rate, the thermocouple nearest to the chill showed an inflection below the liquidus temperature and then cooled to 527° C., well below the solidus temperature for the alloy (545° C.), finally registering a sudden rise to 551° C., above the solidus temperature. The latter inflection is much too large to be accounted for by undercooling of the residual eutectic liquid, and the effect is attributed to a drawing away of the ingot from the chill face with consequent reheating of the solidified portion by conduction from the centre. No other cooling curve showed this feature to the same extent, but two other ingots showed a reduction in the rate of cooling near the chilled face after the temperature had fallen to about 500° C.

The isothermal curves deduced from the cooling curves are reproduced in Figs. 5-7. They are drawn for solidus and liquidus temperatures in each case. A horizontal line drawn through the point on the ordinate representing any particular time after quenching will show the proportions of the ingot in the solid, liquid, and intermediate states at that time. For rapid cooling the lines are close together, and not more

than about a third of the ingot is in the solid-plus-liquid state at any one time. Slow cooling allows a much greater proportion of the ingot to be in this state, and from Fig. 5 it can be seen that after 6 min.

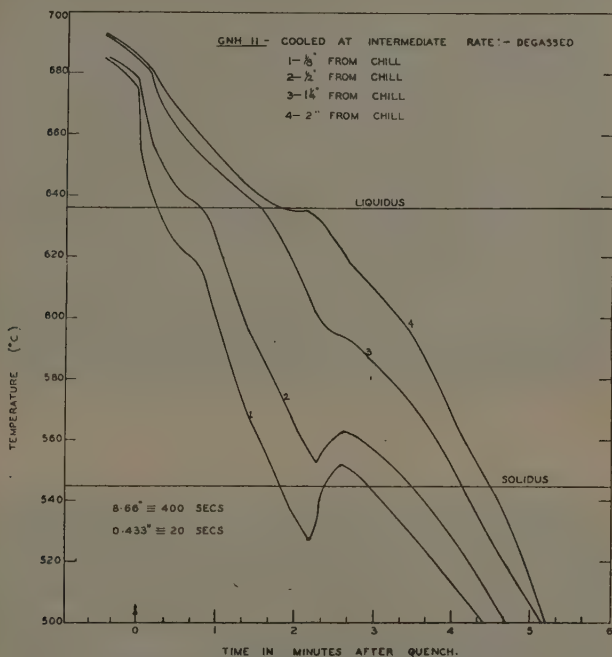


FIG. 4.—Cooling Curves for Aluminium-7% Copper Alloy, Cooled at Intermediate Rate.

practically the whole of the slowly cooled ingot was in the pasty state. Discontinuities in liquidus isothermal curves are generally due to the long times of arrest and super-cooling recorded by thermocouples furthest from the chill.

(b) Macrostructure and Porosity.

Macrostructures of aluminium-3% copper ingots quickly and slowly cooled are illustrated in Figs. 9 and 10 (Plate CIV). These are typical of both the 3%- and the 7%-copper alloys, and show that rapid cooling gave rise to long narrow columnar crystals, while slower cooling produced wide columnar crystals in about a third of the ingot, with

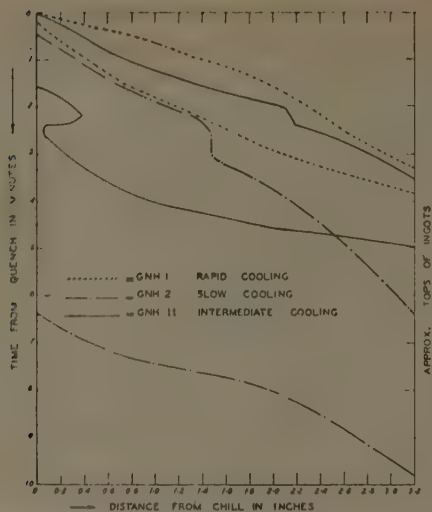


FIG. 5.—Solidus and Liquidus Isothermals for Aluminium-7% Copper Alloys, Degassed.

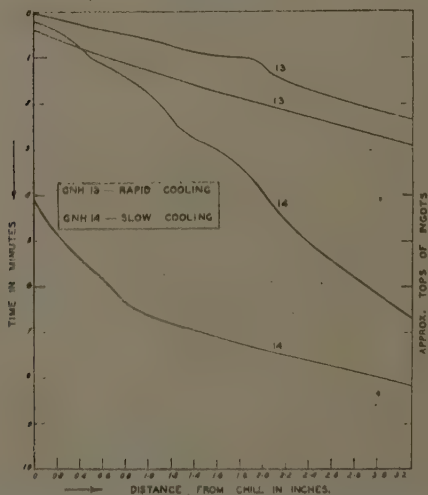


FIG. 6.—Solidus and Liquidus Isothermals for Aluminium-3% Copper Alloys, Degassed.

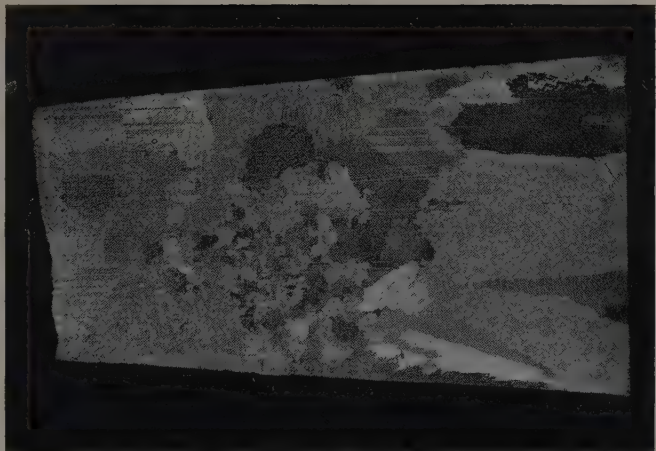


FIG. 10.—Aluminium-3% Copper Alloy Ingot (GNH 16), Slowly Cooled. $\times 1$.

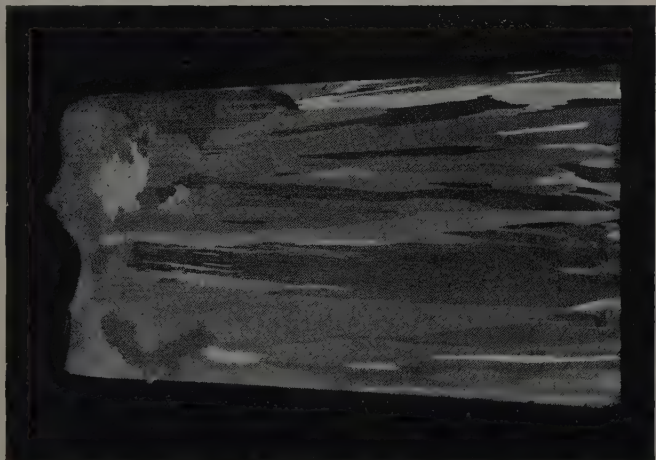


FIG. 9.—Aluminium-3% Copper Alloy Ingot (GNH 17), Quickly Cooled. $\times 1$.



FIG. 11.—Aluminium-7% Copper Alloy Ingot (GNH 28), Grain Refined and Slowly Cooled. $\times 1$.

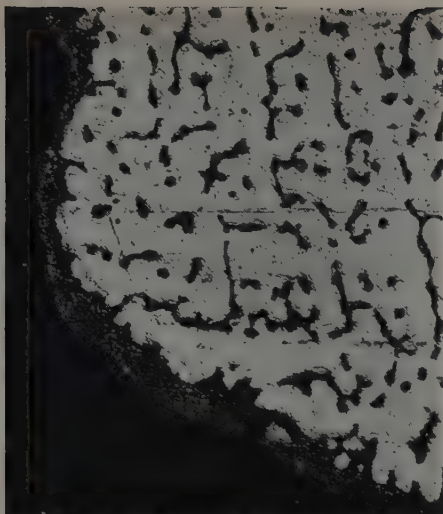


FIG. 12.—Bottom Corner of Aluminium-7% Copper Alloy Ingot (GNH 1), Degassed, Quickly Cooled. $\times 200$.



FIG. 13.—Chill Face of Same Ingot as Fig. 12. $\times 200$.

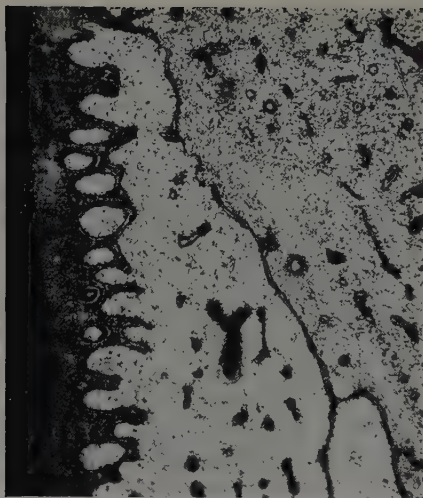


FIG. 14.—Side of Same Ingot as Fig. 12, $\frac{5}{16}$ in. from Chill. $\times 200$.

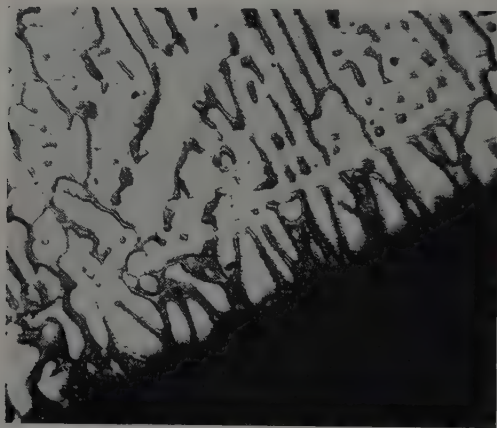


FIG. 15.—Chill Face of Aluminium-7% Copper Alloy Ingot (GNH 8), Gassy, Slowly Cooled. $\times 50$.

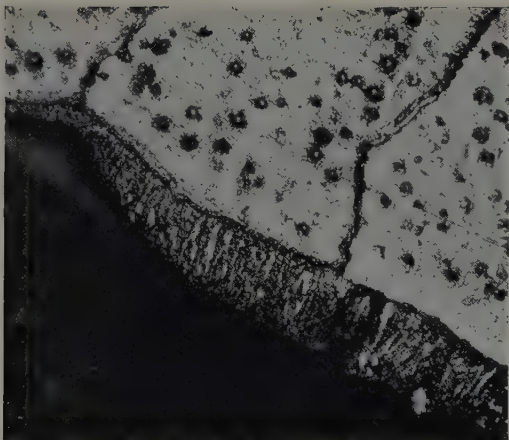


FIG. 16.—Chill Face of Aluminium-7% Copper Alloy Ingot (GNH 9), Quickly Cooled, Gassy. $\times 200$.

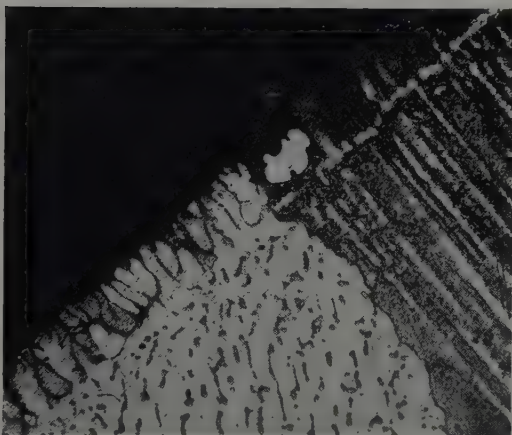


FIG. 17.—Chill Face of Aluminium-7% Copper Alloy Ingot (GNH 11), Degassed, Cooled at Intermediate Rate. $\times 50$.

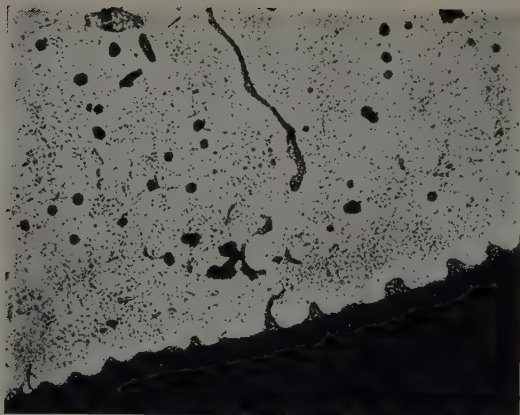


FIG. 18.—Chill Face of Aluminium-3% Copper Alloy Ingot (GNH 13), Degassed, Quickly Cooled. $\times 200$.



FIG. 19.—Same Ingot as Fig. 18. Side of ingot $\frac{5}{16}$ in. from chill. $\times 200$.

equi-axial crystals in the upper portion. The ingot which had been cooled rapidly *in vacuo* was columnar to the top. Treatment of the melt with grain-refining flux gave a uniformly fine-grained structure, whether the ingot was rapidly or slowly cooled; an example is reproduced in Fig. 11 (Plate CV).

Low-power macro-examination revealed voids which had the appearance of true shrinkage cavities caused by a deficiency of feeding liquid, except in the gassy 7%-copper ingots where more rounded holes were

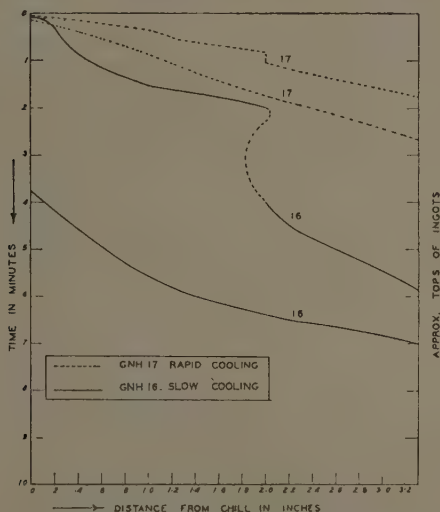


FIG. 7.—Solidus and Liquidus Isothermals for Aluminium-3% Copper Alloys, Gassy.

found in parts more than 1 in. from the chill face. The gassy 3%-copper ingots showed no holes attributable with certainty to gas, nor was there any significant difference in the results of the density measurements, in spite of the fact that the gassy melts had a high gas content and, as with the 7% alloy ingots, bubbles of gas had been observed escaping from the top surfaces of the ingots during solidification.

(c) Microstructure.

Photomicrographs of the base and sides of the degassed 7%-copper alloy that had been quickly cooled, are reproduced in Figs. 12-14 (Plates CVI and CVII). The presence of a eutectic film on the chill

face, and extending for about 2 in. up the sides, is clearly shown. It was of varying thickness, averaging about 0.005 in. on the chill face, and on the sides it showed a marked toothed structure. In some cases the films on the sides had a smooth edge in contact with the body of the ingot. The more slowly cooled ingots had a eutectic film on the chilled face, but no appreciable amount on the sides.

The structure at the chilled face of 7%-copper ingots cooled at slow, rapid, and intermediate rates is shown in Figs. 15, 16, and 17 (Plates CVII and CVIII) (note different magnifications). Inter-

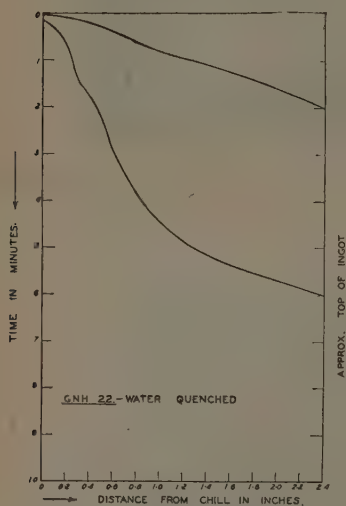


FIG. 8.—Solidus and Liquidus Isothermals for Bismuth-6% Tin Alloy.

crystalline residual eutectic was often continuous with the eutectic films (see, for example, Figs. 13 and 16), giving strong evidence that feeding had taken place through intercrystalline channels. At the chill face there was often a narrow band poor in eutectic between the eutectic film and the body of the ingot (see, for example, Figs. 13 and 15).

The presence of gas was not essential to the formation of eutectic layers, because both the degassed ingots and the ingot solidified *in vacuo* had eutectic layers. Grain refining did not produce any essential difference in the structure at the surface. The eutectic was more intercrystalline, with narrow channels continuous between the grains.

Turning now to the 3%-copper alloys, the general structure is illustrated in Figs. 18 and 19 (Plate CIX), which show sections at the chill face and side of a quickly cooled degassed ingot. There was little residual eutectic within the crystal grains, but there were some eutectic-filled intercrystalline channels (Fig. 18) and at the chill face a thin eutectic layer. For 2 in. up the sides there was a thicker, irregular layer (Fig. 19). In view of the small amount of residual eutectic in the alloy the extent of the eutectic film at the surface is remarkable. A slowly cooled ingot of this composition showed no regular film at the

base or sides, but there was a slight enrichment in eutectic at the base. In micrographic appearance the gassy 3%-copper ingots were similar to the degassed ones.

In these unidirectionally solidified ingots no effects on the eutectic layers can be attributed with certainty to the action of gas, but it is known that, in practice, with symmetrically cooled ingots the amount of exuded eutectic increases with the gas content of the melt.

With regard to the effect of the position of the chill it was shown in earlier, unpublished work of the B.N.F.M.R.A. that the eutectic layer was thicker when the chill was at one side of the mould, instead of at the base, and the ingot could more readily draw away from it during solidification; the layer was absent when the chill was placed centrally so that the solidifying metal shrank on to it.

Summarizing the work on the microstructure of unidirectionally solidified aluminium-copper alloys, it may be said that it is usual to find a film of eutectic, or a layer rich in eutectic, at the chill face. This layer extends up the sides near the chilled face of the quickly cooled ingots. The eutectic layers are often directly connected with eutectic-filled intercrystalline channels, and just inside the layer there is often a narrow band, poor in eutectic. In these particular ingots the presence of gas did not affect the eutectic layers.

(d) *Segregation : Definition of Terms.*

The formation of a copper-rich layer at the chill face has a pronounced effect upon the composition of the first slice cut from the ingot nearest to the chill. In the present paper an estimate of the extent of this effect is made and a distinction is drawn between the general segregation in the body of the ingot and the surface effect resulting from the eutectic layers. The terms that will be used may be defined as follows :

Exudation. The surface enrichment in copper in a layer at the chill face will be referred to as the exudation.

"General" Segregation. This is defined as the difference between the maximum and minimum values of copper content in any ingot, after allowance has been made for the effect of the exuded layer upon the copper content of the first thin slice adjoining the chill face.

The exuded layer is allowed for by estimating its composition and thickness metallographically and then calculating, from the data so obtained and from the analysis of the whole slice, the copper content of the remainder of the slice.

"Positive" Segregation is defined as the maximum enrichment in copper, above the average, towards the chill face; again after allowing

for the effect of the exuded layer upon the composition of the first slice adjoining the chill.

"Corrected" Analysis Curves. In discussing the results it has sometimes been useful to calculate what the composition would have been within the ingot if the feeding had been perfect, i.e. all the voids are supposedly filled with feeding liquid. The results are presented as "corrected" analysis curves. The method of calculating corrected analyses is outlined in the Appendix to the present paper (p. 837).

(c) *Variations in Composition, Density, and Porosity Within the Ingots.*

Curves illustrating the segregation effects are reproduced in Figs. 20-25, where density, actual copper content, "corrected" copper con-

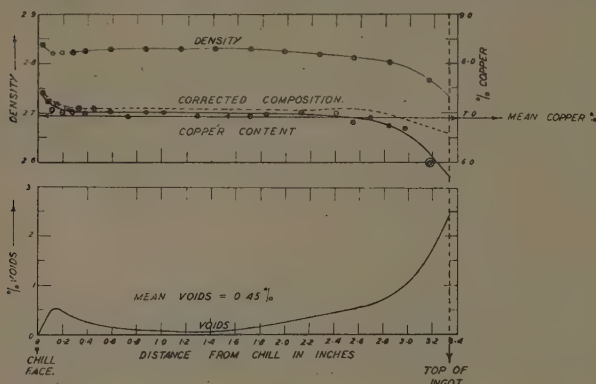


FIG. 20.—Segregation in Ingot of Aluminium-7% Copper Alloy (GNH 1), Quickly Cooled, Degassed.

tent (see definition above), and voids % are plotted against distance from the chill face. To avoid congestion the experimental points have been omitted from all except the first curve.

The "positive" segregation was determined, as described above, for each ingot, and the results obtained are given in Table I. With four exceptions, the adjustment to the copper content of the first slice was of the order of 0.1-0.2% copper, and the adjusted values fell on smooth curves connecting the copper contents of the slices further into the ingot. In these cases the "positive" segregation could be determined with a fair degree of accuracy. In four cases the adjusted copper content of the first slice was still much higher than that of the adjacent slice (GNH 11, 8, 14, and 28 in Table I). These included the two cases where

the exuded layer was very thick and the adjustment was correspondingly large and presumably less accurate. In all these four instances

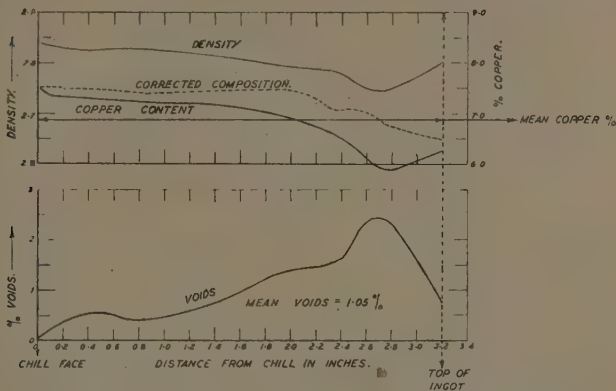


FIG. 21.—Segregation in Ingot of Aluminium-7% Copper Alloy (GNH 2), Slowly Cooled, Degassed.

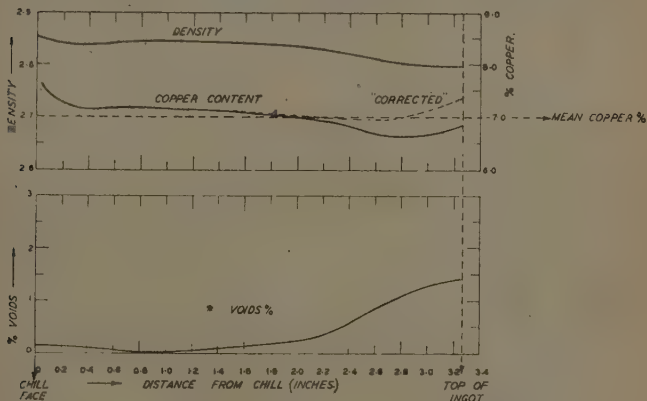


FIG. 22.—Segregation in Ingot of Aluminium-7% Copper Alloy (GNH 27), Quickly Cooled, Grain Refined, Degassed.

the curves connecting the copper contents of the slices within the ingots were extrapolated to the chill face and the "positive" segregation was determined from these curves.

With this adjusted value for the copper content at the chill face the "general" segregation (see explanation above) can be written as the

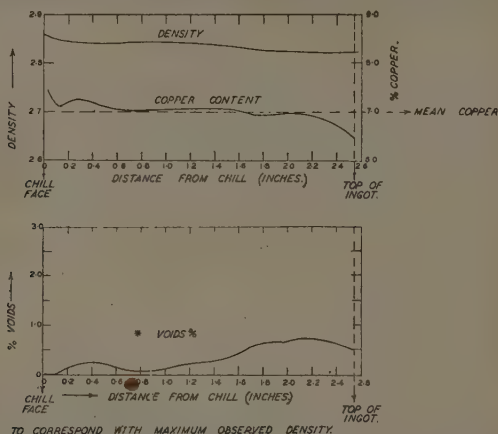


FIG. 23.—Segregation in Ingot of Aluminium-7% Copper Alloy (GNH 38), Vacuum Quenched, Quickly Cooled, No Pre-Solidification.

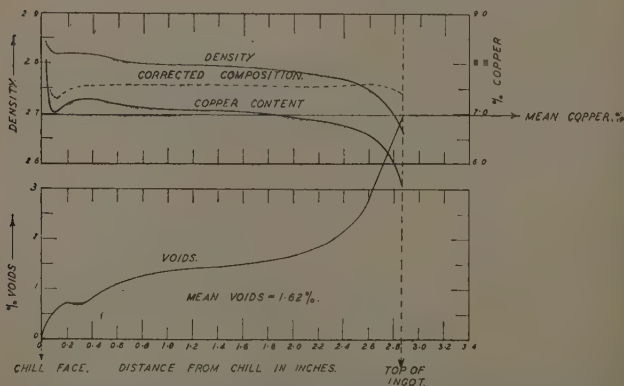


FIG. 24.—Segregation in Ingot of Aluminium-7% Copper Alloy (GNH 9), Quickly Cooled, Gassy.

difference between this figure and the copper content at the top of the ingot or at the minimum point in the curve of composition.

To avoid repetition, the summary and discussion of these results has

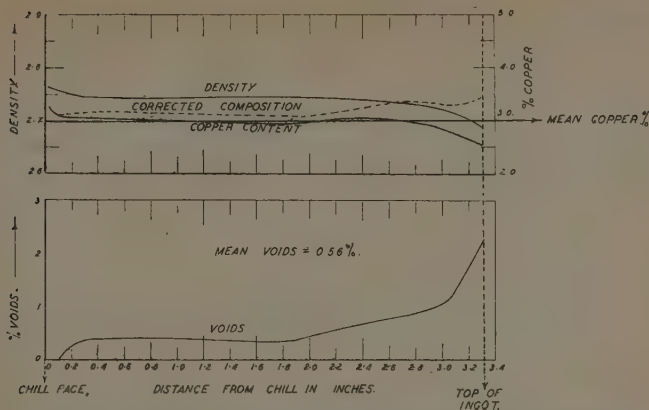


FIG. 25.—Segregation in Ingot of Aluminium-3% Copper Alloy (GNH 13), Quickly Cooled, Degassed.

been deferred to Sections V and VI below. The most significant finding was that the effects of segregation in unidirectionally solidified ingots could be confined to a narrow zone at each end by rapid chilling and promotion of feeding (see, for example, Figs. 20 and 25).

IV.—ADDITIONAL EXPERIMENTAL WORK.

1. Segregation in a Tin-Bismuth Alloy Solidified in One Direction.

If the movement of residual liquid through interdendritic channels during solidification, and hence the segregation, is determined primarily by the solidification shrinkage in aluminium-copper alloys, it becomes of interest to examine an alloy which *expands* on solidification. This property is shown by bismuth, which expands by about 3% on changing from the liquid to the solid state, and by alloys having bismuth as the main constituent. The binary alloy of bismuth with 6% tin has a freezing range not very different from that of an aluminium-7% copper alloy, and, as the tin-bismuth system is a simple eutectic, bismuth-rich primaries will be formed during solidification, together with eutectic containing 42% tin. The bismuth-6% tin alloy was therefore selected for unidirectional solidification tests on an alloy which expands on solidification.

To obtain an ingot solidified in one direction the same apparatus was used as for the aluminium-copper alloys, with the base-plate chilled by means of a jet of water as before. The temperature gradient in the bismuth-tin alloy was steeper than that in the aluminium-copper alloys

cooled under the same conditions, because bismuth has a much lower thermal conductivity. This effect is shown in the isothermals for the bismuth-tin ingot, reproduced in Fig. 8, by the wide angle between the lines near the chill face.

The ingot was sound and there was no surface film on the chilled face or on the sides. Crystals were columnar for about 1 in. from the chill, and above this they were equi-axial. With increasing distance

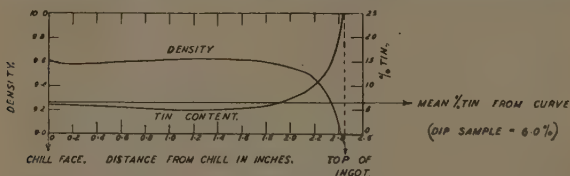


FIG. 26.—Segregation in Ingot of Bismuth-6% Tin Alloy, Water Cooled.

from the chill the eutectic areas increased rapidly in size, until they were visible to the naked eye near the top. For about 0.1 in. from the top the eutectic was almost continuous, suggesting exudation upwards.

A centre stem was cut from the ingot and examined in slices as before, variations in composition near the top of the ingot being studied more closely than usual. Curves showing the changes in composition and density are reproduced in Fig. 26. The curve for tin content does not indicate any appreciable change at the chill face. The density curve indicates a slight "normal" segregation over the first 0.2 in. from the chill.

In the $\frac{1}{2}$ in. furthest from the chill there is a rapid increase in tin content and decrease in density. Thus the segregation in the ingot was "normal", i.e. tin content increasing in direction of crystal growth.

2. Segregation in Aluminium-Copper Alloys Chilled from the Top.

A horizontal open disc 0.5 in. thick was made in a pre-heated carbon mould by cooling the top surface with a heavy plunger. Several similar discs were also made by chilling from below, either in the original mould or by means of a heavy block of copper.

Duplicate analyses of samples taken at different distances from the chilled face gave the following average results :

Distance from chill face, in.	1/16	3/16	5/16	7/16
Copper content, %	7.2	7.16	6.87	6.70

The chilled face had a well defined layer rich in eutectic, which, however, was not thick enough to affect materially the copper content of the first slice.

The results show that cooling from the upper face gave substantially the same variations in composition near the chill face as were observed in the ingots cooled from the base.

3. *Very Slow Unidirectional Cooling of Aluminium-Copper Alloys.*

In order to extend this investigation of segregation to conditions of very slow unidirectional cooling, two further experiments were carried out.

In the first, a mould containing the alloy was lowered at a rate of 2 in./hr. through a vertical furnace. The mould was of carbon, 3 in. long, 1 in. in dia., and tapered (45° half angle) to a point at the base. Degassed aluminium-7% copper alloy was used and an atmosphere of nitrogen was maintained during the experiment. The temperature difference between the two ends of the alloy did not at any time exceed 8°C .

The casting consisted of a few large columnar crystals with their long axes parallel to the long axis of the casting. Samples representative of various levels above the base were analysed for copper content with the following results :

Distance above base, in.	. . . $\frac{1}{16}$. . . $\frac{3}{16}$. . . $\frac{5}{16}$. . . $\frac{7}{16}$. . . $\frac{11}{16}$. . . $\frac{14}{16}$. . . $\frac{19}{16}$
Copper content, %	. . . 7.98	. . . 7.09	. . . 7.3	. . . 7.4	. . . 7.37	. . . 6.99	. . . 6.59
Distance above base, in.	. . . $\frac{23}{16}$. . . $\frac{27}{16}$. . . $\frac{31}{16}$. . . $\frac{35}{16}$. . . $\frac{39}{16}$. . . $\frac{43}{16}$	
Copper content, %	. . . 6.60	. . . 6.54	. . . 6.62	. . . 6.63	. . . 6.60	. . . 6.80	

In the second experiment the specimen was held in an alumina pot at a fixed position inside a heating tube, with a vertical temperature gradient such that the top of the melt was 2° - 3°C . hotter than the base. The heating current was slowly reduced, so that the alloy took 3 hr. to cool from liquidus to solidus temperature.

The casting contained a few small crystals at the base and at the extreme upper surface, the remainder consisting of a single crystal. Samples taken from a piece $\frac{3}{16}$ in. square cut from the long axis of the casting had the following copper contents at the indicated levels above the base :

Distance above base, in.	$\frac{1}{16}$	$\frac{5}{16}$	$\frac{9}{16}$	$\frac{13}{16}$	$\frac{17}{16}$	$\frac{21}{16}$	$\frac{25}{16}$	$\frac{29}{16}$	$\frac{33}{16}$	$\frac{37}{16}$
Copper content, %	7.08	5.97	5.69	5.74	5.83	5.79	6.04	6.41	6.43	6.30

Thus both the slowly cooled castings displayed enrichment in copper near the base, suggestive of gravitational draining of copper-rich liquid, and above this region "normal" segregation had occurred, the copper content increasing in the direction of crystal growth, this being most marked in the second casting.

4. *Rapid Unidirectional Cooling of Longer Castings.*

The work on unidirectionally cooled aluminium-copper alloys had shown that a casting substantially free from segregation could be produced by solidifying progressively from one end and then cutting off the narrow zone in which the segregation is concentrated. To confirm this, two experiments with aluminium-7% copper alloy were carried out.

In the first a 2-in.-dia. steel tube, 8 in. long, was lagged with fireclay of thickness tapering from $1\frac{1}{2}$ in. at the top to $\frac{1}{2}$ in. at the base. This mould was pre-heated to about 800° C., and placed on a copper slab cooled on the underside with a jet of water. The alloy was poured quickly to a depth of 2 in. in the mould and then the rate of pouring was controlled so that as the ingot solidified from the base upwards the liquid layer was

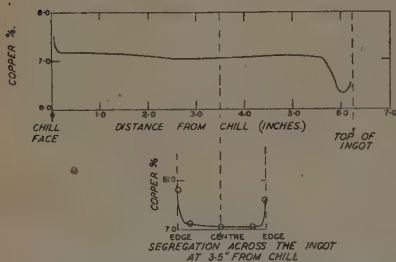


FIG. 27.—Ingot Cast in Pre-Heated Mould and Chilled from One Face. Time of pouring: 12 min. Ingot length $6\frac{1}{4}$ in.; ingot dia. $1\frac{13}{16}$ in.

maintained at about $\frac{1}{2}$ in. depth. At distances of more than a few inches from the chill the cooling became very slow. The pouring time for an ingot 6 in. long was 12 min.

In the second experiment the mould was a steel tube of $1\frac{1}{2}$ in. dia. with a steel plate welded to the base. Again it was pre-heated to 800° C. The molten alloy was poured into the mould and the whole lowered slowly through a furnace so arranged over a water bath that only a very short space separated the furnace from the cold water. An ingot 7 in. long was solidified in about 2 min.

The variations in actual copper content in vertical and horizontal planes in these two castings are illustrated by the curves reproduced in Figs. 27 and 28. By discarding thin slices from the ends both ingots could be rendered almost free from segregation in a vertical direction. There was enrichment at the sides of the first ingot, due to exudations, and only slight enrichment at the sides of the second.

5. *Symmetrically Cooled Sand Castings.*

Three sand-cast blocks were made from aluminium-7% copper alloy. The first was poured at a little below 700° C., into a green-sand

mould to form a cylindrical block 3 in. in dia. and 3 in. high; finely divided green sand was sprinkled deeply on the top immediately after pouring, so that the block cooled symmetrically. The second was cast at about 800° C., into a dry-sand mould pre-heated to about 200° C., and hot dry sand was placed on the top; this method gives a much slower rate of cooling than the first. The third was a 2-in. block cast similarly to the second.

In the first block cast in green sand, the segregation was inverse, with maximum copper contents, averaging 7.2% copper, at the corners

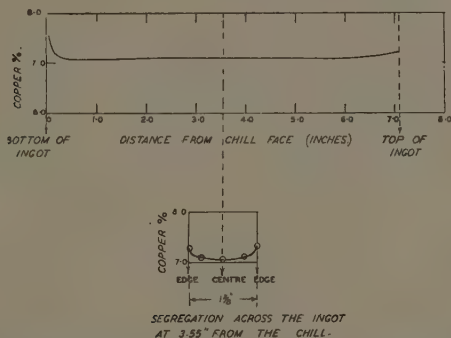


FIG. 28.—Ingot Cooled by Lowering Steel-Tube Mould, Containing All the Melt, Slowly into Water. Time of lowering: approx. 2 min. Ingot length $7\frac{1}{8}$ in.; ingot dia. $1\frac{3}{8}$ in.

and with copper contents ranging from 6.3 to 6.8% near the centre. The fine-grained macrostructure did not give much indication of the direction of crystal growth. The slight porosity was more pronounced in the central regions.

The segregation in the 3-in. block cast in pre-heated dry sand was quite different. There were well marked areas of enrichment towards the centre and base, which reached a maximum of nearly 1.5% copper near the centre of the base. There was impoverishment at the top and sides and the surface was rough, showing projecting dendrites very clearly and indicating a movement inwards of residual liquid. Large single crystals were separated by areas of small ones and there was considerable porosity in the body of the ingot, especially a little below the centre. In the 2-in. block, also cast in pre-heated dry sand, there was copper enrichment in a region a little below the centre, reaching a maximum of about 1%.

6. *Gravitational Segregation.*

In carrying out the experiments on directional solidification *in vacuo* two of the ingots were pre-solidified and remelted in the vacuum furnace. The heating was carried out indirectly by radiation from an iron tube, itself heated by the induction coil. The presence of this iron tube prevented the stirring action of the current on the molten aluminium alloy, so that any gravitational segregation taking place on remelting would persist.

Examination of the resulting ingots showed a great enrichment in copper near the chill face; the copper content increased towards the chill face from 7 to nearly 9.5% over about 0.3 in. Without pre-solidification the enrichment at the chill face was much less, as previously described. The explanation of these results is to be found in the gravitational segregation of the copper-rich liquid towards the base on remelting under quiescent conditions. The same effect has been noticed by Phillips and Brick.⁵ Such gravitational effects may occur either during melting or during a slow solidification in certain cases.

V.—SUMMARY OF RESULTS.

The main results of this investigation of segregation in aluminium-copper alloys containing 3 and 7% copper may be summarized as follows :

(1) Copper segregates inversely in ingots solidified unidirectionally at widely different rates. This effect was found in ingots formed by chilling a quiescent melt from above or below, and also in those formed by pouring metal on to a chill plate. Only with extremely slow cooling is "normal" segregation produced in unidirectionally solidified ingots of these alloys.

(2) Exuded eutectic or eutectic-rich layers were formed at the chill face of these ingots, both when they were chilled from the base and when they were chilled from the top. Rapid chilling from the base caused the exuded layer to extend up the sides of the ingot. Exudations were not eliminated by grain refinement nor by solidifying in a vacuum, nor were they affected by gas content under these conditions. It was found that if the contact between chill plate and ingot was broken during the early stages of solidification, the chill face of the ingot became pasty again as a result of reheating from the body of the metal, and allowed the passage of liquid into the space. A bismuth-6% tin alloy, which expands on solidifying, did not form exudations at the chill face when it was unidirectionally cooled; normal segregation occurred in this ingot.

(3) Just inside the eutectic or eutectic-rich layer it was usual to find a narrow band poor in eutectic.

(4) The maximum enrichment near the chill face, after adjusting for the effect of exudation, has been called the "positive" segregation. It was found that the *magnitude* of this enrichment was not critically dependent upon rate of cooling, but at the same time rapid cooling gave an ingot in which the enrichment was confined to a narrow zone near the chill, while slower cooling caused the zone to extend further into the ingot.

(5) At the end away from the chilled face there was a region impoverished in copper. The extent of this region depended upon the nature of the crystal growth and was less sharply defined than the enrichment towards the chilled face. In slowly cooled ingots the areas of enrichment and impoverishment overlapped, so that there was a gradual change in composition throughout the whole length, whereas rapid cooling gave ingots in which the effects of segregation were confined to the two ends.

(6) The release of dissolved gases and the action of gravity had little effect upon the segregation in these unidirectionally cooled ingots, although it is known that the former is important in symmetrically cooled castings.

(7) A small maximum in the porosity curve was regularly found within about $\frac{1}{2}$ in. of the chill face and then, after a decrease in the centre of the ingot, the porosity increased towards the end away from the chill. Rapid cooling gave lower total voids per cent. than slow cooling. Solidifying in a vacuum made the porosity more uniform, and grain refinement brought about a slight reduction in total porosity.

(8) In sand-cast blocks, cooled from all sides, the segregation was reversed when the rate of cooling was reduced; rapid cooling in green sand resulted in inverse segregation, while slower cooling in pre-heated dry sand resulted in "normal" segregation.

VI.—DISCUSSION OF RESULTS.

1. *Theory of Segregation in Directionally Solidified Ingots.*

It is believed that the main features of the segregation recorded in the present work can be accounted for by the consideration of a simple feeding of residual liquid into the region solidifying. Such simple evidence as the sinking of liquid from between the dendrites at the exposed top of a directionally solidified casting shows that such a feeding movement occurs. The way in which voids are distributed in degassed aluminium-copper alloys also indicates a simple process of

feeding of residual liquid to compensate contraction on solidification. When alloys which expand on solidification are chilled from the base the upward feeding and exudation of residual liquid can be observed, and the reversal of the direction of segregation in the ingot has been confirmed.

With the present closely defined conditions of experiment it should be possible to predict the main features of segregation, if a simple feeding mechanism is an adequate basis for the explanation.

Consider the idealized case represented in Fig. 29. An ingot is represented as solidifying at a constant rate from the bottom upwards, a constant distance of one-eighth of the total length of the ingot being maintained between the solidus and liquidus levels. Crystallization starts at centres at the chill face *C*, and the relative amounts of liquid and solid are shown diagrammatically by different shading for various stages in the growth of the ingot—(*b*) to (*h*). Diffusion in a vertical direction within the liquid phase will be ignored; this is justified for all moderately rapid cooling rates in circumstances where residual liquid is contained in intricate intercrystalline and interdendritic channels. The feeding of liquid between the growing crystals to compensate for solidification contraction is assumed to be perfect.

As the crystals grow upwards from (*a*) they thicken (*b*) and at (*c*) the chill face from which the growth began has reached the solidus temperature. Meanwhile, residual liquid feeds downwards, to compensate for freezing shrinkage, and as it traverses the solid + liquid region its temperature is lowered and it becomes enriched in the segregating element. Thus, in (*b*), the liquid which reaches the chill face has already become enriched, and the concentration of the segregating element at the chill face increases progressively until the solidus temperature is reached (*c*). Since diffusion across the liquidus level is assumed to be zero, the liquid feeding downwards into the solidifying zone at this level, to replace the enriched liquid moving towards the solidus level, will have the same composition as the original liquid. Hence the upper part of the solidifying layer will be impoverished in the segregating element, as shown by the curve of composition in the Figure. As solidification proceeds from (*c*) to (*d*), the impoverished region receives in its turn an enriched feeding liquid and another impoverished region forms above it. This process repeats itself until the impoverished region occurs at the top of the ingot. Complete feeding of this last zone is impossible, but in this ideal case there will be only a narrow layer at the top where feeding liquid fails, and the composition will fall sharply to that of the first deposited solid—the tips of the projecting dendrites.

On this theory the main features of segregation will be an increase

in the amount of the segregating element in the region of the chill face, the width of the enriched zone being determined by the distance from the chill face to the liquidus isothermal at the moment when the chill face reaches the solidus temperature, together with a more sharply marked decrease near the top of the ingot.

In any practical case imperfect feeding will cause a rounding off of

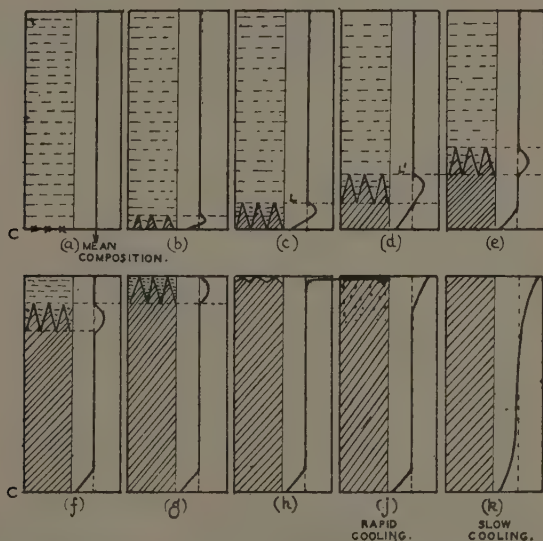


FIG. 29.—Representation of Crystal Growth in a Unidirectionally Solidified Ingot.

the fall at the top—from (h) to (j) (Fig. 29). For rapid cooling there will be a flat portion on the composition curve, the segregation being confined to regions near the top and bottom (j); but for slower cooling the temperature gradients are more gradual, the freezing zone is wider, and the horizontal portion of the curve tends to disappear (k). This general feature of the effect of cooling rate can be seen in the experimental curves.

Experimental isothermal curves show that as crystallization proceeds the depth of the solidifying zone increases considerably, the temperature gradients becoming less steep at greater distances from the chill (see, for example, Fig. 5). This condition is represented diagrammatically in Fig. 30. The chill face C is being fed continually with enriched liquid during the comparatively rapid transition to (b). But

if this feeding has taken place very quickly the liquid which has travelled downwards may not have had time to attain its maximum enrichment and the enrichment at the chill face may be rather less than for a slower cooling. The layer LL' is impoverished to the extent that CL is enriched, but during the slower growth from (c) to (d) the layer LL' may attain a final composition slightly richer in the segregating element than the mean composition of the alloy. The final distribution may thus be as shown at (e), and Fig. 20 shows an experimental curve of this type.

Thus the distribution of the "positive" segregation (the enrichment towards the chill face allowing for surface eutectic) in the experimental curves can be explained quite well on this simple theory.

Conditions at the top of the ingot do not allow of any precise formula-

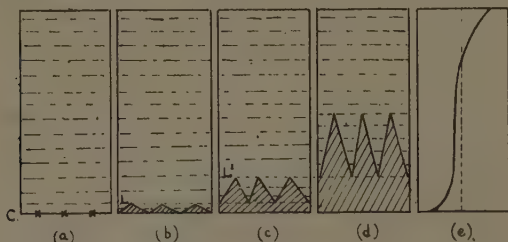


FIG. 30.—Representation of Change in Depth of Solidifying Zone during Directional Solidification.

tion of the extent of the impoverishment to be expected. The actual magnitude of the impoverishment will depend on the completeness or otherwise of feeding, and with slowly cooled or grain-refined ingots independent crystallization at the top of the ingot will also have an effect. Such crystallization may hinder feeding at some stage represented at (g) in Fig. 29, causing the maximum impoverishment to be removed some distance from the top, and the feeding downwards of liquid together with small independent crystallites affects the curve in the same way. This mass feeding downwards of a pasty mixture of liquid and solid could be seen in the tops of grain-refined ingots, and the experimental curves showed that in the slowly cooled ingots, both with and without grain refining, there was a maximum in porosity removed some distance from the top (e.g. Fig. 21) and a corresponding minimum in the curve of composition. The same tendency was also shown by the quickly cooled grain-refined ingot (Fig. 22), confirming that spontaneous crystallization is responsible. With grain refinement the impoverishment in copper towards the top was less marked, giving a

smaller "general" segregation (Table I). The "positive" segregation towards the chill face was not affected by grain refinement.

The idea of a simple feeding process is supported by the "corrected" analysis curves obtained from the quickly cooled ingots; these ingots were persistently columnar. If the voids in an ingot which has grown progressively from bottom to top are filled with liquid of eutectic composition the "corrected" analysis curve should remain flat, or else rise above the average composition where the voids are more numerous. This result was found experimentally (see Figs. 20-25).

It has been shown that the impoverishment towards the top of an ingot is an indeterminate quantity, but if the simple theory presented above is adequate, it should be possible to make estimates of the correct order for the magnitude of the "positive" segregation. For equilibrium conditions Masing and Haase⁶ took the average composition of the feeding liquid as that composition in equilibrium when the amounts of solid and liquid are equal. Under conditions of rapid cooling this will not apply; it has been shown, for instance, that there was an appreciable amount of residual eutectic in the ingots with 3% copper. To arrive at a theoretical value for "positive" segregation under the present conditions of experiment, an approximate estimate was made microscopically of the amount of residual eutectic. Alloys with 7% copper showed about 10% of eutectic, and alloys with 3% copper about 3% of eutectic. The feeding is regarded as taking place in the two stages—during the cooling to the eutectic temperature and during the final solidification at the eutectic temperature. The average copper content of feeding liquid during the first stage will be rather greater than the value at the point where liquid and solid are equal in amount, but cannot be as great as twice the average copper content, modifying the Masing and Haase conception by a simple depression of the solidus. Thus for alloys with 7% copper the value may be taken as between 12 and 14% copper, and for 3%-copper alloys between 5 and 6%. The contraction during solidification of the eutectic is supposed to be fed with liquid of eutectic composition.

The maximum enrichment in the present ingots with 7% copper can be estimated as the feeding of the 6% solidification contraction in the two stages:

5.4% voids filled with liquid containing 13% copper.

0.6% voids filled with liquid containing 33% copper.

Using formula (1) from the Appendix these values give respectively 0.36 and 0.22%, the maximum enrichment thus being 0.58% of copper.

For alloys with 3% copper, 5.8% contraction is considered to be fed

with liquid containing 5.5% copper, and 0.2% with liquid containing 33% copper. The total enrichment in this case is calculated to be 0.23% copper.

The average values of the "positive" segregation in the two cases were found to be 0.5 and 0.25%, respectively.

In the above-stated argument continuous feeding of residual liquid has been assumed. The low percentage of voids near the chill face of the ingots suggests uninterrupted feeding, but the maximum in the curve of porosity generally found within 0.5 in. of the chill face may indicate some discontinuity in the process. In cases where there had been any discontinuity, values of "positive" segregation higher than those calculated above could be expected, for the voids may be filled at a fairly late stage with liquid considerably enriched in copper. On the other hand, lower values of "positive" segregation may occur if the feeding is imperfect or if a heavy exudation has occurred; for example, less perfect feeding *in vacuo* (GNH 38) and heavy exudation (GNH 8 and GNH 9—Table I).

To complete this Section on the general theory of the process and the effects of rate of cooling, it remains to consider the results to be expected under conditions of very slow cooling. Only in special cases can cooling be very slow and crystal growth be maintained unidirectional, and two such cases have been described in Section IV. 3. The solidification occupied several hours, and under such conditions the assumption made in the above theoretical discussion—that diffusion between the liquid region and the enriched liquid in the solidifying zone could be neglected—is not justified. Phillips and Brick⁵ have shown that diffusion in such a case will be very slow but quite appreciable over a number of hours. It is obvious that if such diffusion within the liquid phase becomes appreciable the ingot may exhibit a "normal" segregation, the liquid last to solidify being enriched above the average in the segregating element. If diffusion were perfect in both liquid and solid phases there would, of course, be perfect equilibrium and no segregation at all; but diffusion in the liquid, although slow, will obviously be more rapid than diffusion in the solid. No estimate can be formed of the magnitude of the "normal" segregation to be expected for various rates of cooling, but the enrichment in the region last to solidify may be considerable. It has already been pointed out that even when the crystal growth is directional the secondary effect of gravitational forces may be apparent, if the cooling is very slow. This is still more marked when cooling takes place from all sides.

2. Factors Determining the Movement of Residual Liquid.

Having found a theory based on the compensation of solidification contraction by the feeding of residual liquid to be adequate to explain the observed effects in unidirectionally solidified ingots of aluminium-copper alloys, it remains to investigate the relative importance of the various factors influencing the movement of the feeding liquid.

There are four factors which may be important: the release of dissolved gases and the exertion of vapour pressure; gravitational forces (density effect); suction into cavities (force of atmospheric pressure); and capillary forces (surface energy effects).

It has been shown that in unidirectionally grown ingots the effects of gas are comparatively slight, gas bubbles readily escaping from the metal as it solidifies. Much more important effects may be expected from gas evolution if the ingot is not grown directionally but as a shell solidifying from the outside.

The experiment with ingots chilled at the top surface showed that gravity was not a deciding factor in ingots cooled moderately rapidly. Gravitational effects were found only after very slow cooling or after remelting and solidifying a second time.

When ingots were cooled *unidirectionally* in a vacuum the segregation was inverse, and although certain features of the segregation were slightly modified it was clear that atmospheric pressure was not a decisive force in the movement of residual liquid.

The evidence given here is not entirely conclusive, but it indicates strongly that in directionally solidified ingots the major force determining the movement of the residual liquid arises from the surface energy of the liquid. These factors do not necessarily operate in exactly the same way if growth is not directional. Such cases are discussed below.

3. Segregation in Symmetrically Cooled Sand-Cast Blocks.

The 3-in. block of aluminium-7% copper alloy which was cooled fairly rapidly in green sand (including the top surface) showed inverse segregation, the maximum enrichment, in the corners, being of the same degree as in the unidirectionally solidified ingots. The conditions in both cases are much the same, except that in the sand-cast block atmospheric pressure may oppose the outward movement of residual liquid until a solid shell is formed, after which this force is inoperative. Surface forces in the narrowing channels in which the eutectic solidifies will necessitate the outward feeding of residual liquid.

With slower cooling in pre-heated dry sand the result was entirely different. There would be little temperature gradient in the metal and solidification would not be strongly progressive from the sides inwards.

In such cases, also, cooling may be sufficiently slow to allow of appreciable diffusion in the liquid phase. The simultaneous action of forces driving enriched liquid inwards, of gravity, and of diffusion in the liquid, is sufficient to explain the experimentally observed enrichment at a maximum between the centre and base of such blocks. While such a segregation may be called "normal" it is not necessarily "normal" relative to the direction of crystal growth. In sand-cast blocks solidifying from all sides the effects of gas are likely to be significant. For example, Slater ⁷ describes how the direction of segregation may be completely reversed with increasing gas content.

VII.—APPLICATIONS.

1. *Chill Castings.*

Cast in the ordinary way into a heavy chill mould aluminium-copper alloys will show inverse segregation near the mould walls, and an impoverishment in the segregating element in the central regions, the extent of the impoverishment depending on the completeness of the feeding. If the conditions are such that the solidifying alloy can shrink away from the mould walls, heavy exudation may be expected. Interlocking of crystals, turbulence during pouring, and gravitational effects in large ingots will complicate the results. The present work has shown that the most desirable method of casting an ingot is to solidify progressively from one end, the segregation then being concentrated in a narrow zone which may finally be cut off.

The various continuous casting processes developed in recent years approach the conditions required to minimize segregation within the ingot, especially those where the metal is poured into a short mould, and a large proportion of the heat is abstracted by cooling water sprayed directly on to the emerging ingot surface. Even in these processes, however, low-melting-point liquid frequently exudes through the surface of the casting and machining is often necessary before working. It is clearly impossible to eliminate exudations from such castings, because some clearance is necessary between mould and ingot to allow the latter to emerge without undue hindrance.

2. *Sand Castings.*

As far as sand castings are concerned the most useful feature of this work is that it throws light on the forces promoting the flow of feeding liquid. A knowledge of the relative importance of the several recognized forces should be of assistance in devising casting techniques which will minimize porosity in castings.

3. Exudations.

The most troublesome forms of inverse segregation in practice are the exudations or "blebs" of low-melting-point constituents on the outside of chill castings. The present work shows that there is little prospect of avoiding these segregates because the only satisfactory remedy is to prevent the formation of gaps between the ingot and the mould, and this is unlikely to be practicable. Whether steps to prevent exudation are justified is a matter of production economics, bearing in mind that exudation must be prevented completely if a machining operation is to be avoided. A point in favour of retaining the machining operation for chill castings intended for working is that this removes not only the exudations but also a large part of the segregation in the portions which solidified first.

ACKNOWLEDGEMENTS.

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APPENDIX.

"CORRECTED" ANALYSIS.

If a simple feeding mechanism is applicable to the theory of inverse segregation in aluminium-copper alloys, it might be considered possible, supposing the voids in the top layers of the ingot to be filled with feeding liquid of appropriate composition, to construct a "corrected" analysis curve which would remain flat in this region. In the present experiments the total voids are only small percentages and it is sufficient to assume eutectic composition for the feeding liquid. If this assumption is not justified then it would be expected that the "corrected" curve would rise towards the top. This argument assumes perfectly directional growth, but if spontaneous crystallization occurs, and if the solid crystallites and residual liquid consolidate themselves by mass feeding, then "corrected" analysis loses its significance. The tendency for "corrected" copper content to remain constant or to show an increase

towards the top of the ingot is generally found to be true for those ingots which are persistently columnar, and also for the shorter ingots (quickly cooled). The evidence given by "corrected" analysis curves is therefore not inconsistent with the general theory developed here.

In calculating "corrected" analyses it must be observed that the density of eutectic is greater than that of the alloy, and the increase in copper content *by weight* has to be calculated. From published data the density of copper-aluminium eutectic with 33% copper is about 3.7 g./c.c. Let observed composition = C_A ; observed density = d_A ; maximum density for alloy $C_A = d_{A_{\max}}$; percentage voids = V ; eutectic composition = C_E ; eutectic density = d_E . Then it can easily be shown that if the voids are filled with alloy of eutectic composition the "corrected" composition can be calculated from either of the formulæ:

$$\% \text{ Copper "corrected"} = \frac{V \left(C_E \cdot \frac{d_E}{d_{A_{\max}}} - C_A \right) + 100 \cdot C_A}{V \left(\frac{d_E}{d_{A_{\max}}} - 1 \right) + 100} \quad (1)$$

or:

$$\% \text{ Copper "corrected"} = \frac{V \cdot C_E \cdot \frac{d_E}{d_{A_{\max}}} + 100 \cdot C_A}{V \cdot \frac{d_E}{d_A} + 100} \quad (2)$$

The first formula uses $d_{A_{\max}}$ which is read directly from a standard curve for the corresponding composition C_A , and is the most convenient formula if only composition and voids are given. The second formula is rather simpler if the actual density has been observed. In general, the first formula is the more useful, as it can be simplified to an approximate form with less loss of accuracy. The factor $\frac{d_E}{d_{A_{\max}}}$ will be of the order of 1.3 for aluminium-copper alloys, and the denominator of equation (1) can be taken as 100 with an error of not more than 1% for voids up to 3%. For alloys in one series, e.g. varying from 6 to 8% of copper in aluminium, $\frac{d_E}{d_{A_{\max}}}$ can be taken as a constant, the variation being only 2%. Also, C_E is a constant—33% copper. Thus we can write (1) as:

$$\% \text{ Copper "corrected"} = \frac{V(43.25 - C_A) + 100 \cdot C_A}{100} \quad (\text{for Al-7\% Cu})$$

and:

$$\% \text{ Copper "corrected"} = \frac{V(44.3 - C_A) + 100 \cdot C_A}{100} \quad (\text{for Al-3\% Cu}).$$

THE EMBRITTLEMENT OF TOUGH-PITCH 1184 COPPER BY BISMUTH.*

By A. P. C. HALLOWES,† B.Sc., A.I.M., MEMBER.

(Communication from the British Non-Ferrous Metals Research Association.)

SYNOPSIS.

It is shown by notched-bar and tensile tests that if bismuth-bearing tough-pitch copper is rapidly cooled from a high temperature (e.g. 800°–900° C.), then cold worked, and finally recrystallized by annealing at a low temperature (e.g. 350°–450° C.), embrittlement occurs at the heat-treatment temperature and persists at room temperature after cooling.

Maximum embrittlement occurs after annealing at 350° C. (the lowest temperature used), but coppers embrittled between 350° and 450° C. regain ductility after longer periods of heating at these temperatures. Alternatively, the embrittlement can be removed by initial annealing at 600° C. prior to lower-temperature treatment. The brittleness is attributed to the precipitation of bismuth at the grain boundaries, and the recovery of ductility is ascribed to the conversion of the bismuth to harmless inclusions of bismuth oxide.

The practical implication of the results is discussed and recommendations are made with a view to avoiding bismuth embrittlement of tough-pitch coppers. With normal grain-sizes of the order of 0.015 mm. ($\sqrt{\text{area}}$) and bismuth contents not exceeding 0.0035%, the embrittlement observed is unlikely to have any practical significance.

I.—INTRODUCTION.

ALTHOUGH it is known that bismuth does not generally cause embrittlement in tough-pitch coppers, certain instances of serious embrittlement have arisen during a general investigation of the effect of bismuth on the properties of coppers. The special conditions in which this embrittlement in tough-pitch coppers has been encountered have been fully investigated, and an explanation of this occurrence is offered in the light of earlier work on bismuth in deoxidized¹ and oxygen-bearing⁵ coppers.

II.—AVAILABLE INFORMATION.

Archbutt and Prytherch,² in discussing the subject of bismuth in copper, reviewed work on copper-bismuth-oxygen alloys by Hampe and by Johnson and described two series of experiments of their own. Hampe reported that bismuth is not so detrimental in the presence of

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oxygen and that bismuth occurs as oxide in copper when an equivalent amount of oxygen is available. Johnson found that copper containing bismuth as bismuth oxide was more malleable than that with the same amount of bismuth alone, and identified four constituents in copper-bismuth-oxygen alloys; in addition to the metallic copper matrix, globules of bismuth, cuprous oxide, and particles of a composite constituent adjoining the cuprous oxide could be seen.

Of the experiments by Archbutt and Prytherch, the first series dealt with materials containing 0.01–0.02% oxygen, with bismuth contents from 0.002 to 0.1%, while in the second the oxygen concentration was increased to between 0.04 and 0.1% with 0.02–0.03% bismuth. In no case was serious embrittlement encountered, but all specimens were tested at room temperature after annealing at 700° C. These results are substantially confirmed by industrial practice.

Blazey³ stated that embrittlement disappeared when the oxygen content of copper was three or four times as great as the bismuth content, but industrial practice suggests that an oxygen : bismuth ratio of 10 : 1 is desirable for this purpose.

In the discussion of a paper by Price and Bailey⁴ on the effect of bismuth on the working properties of brasses, Smart and Smith gave an account of some experiments in which oxygen-bearing as well as oxygen-free coppers were embrittled by bismuth. In copper slugs containing from 0.023% to 0.037% oxygen, no embrittlement was encountered with 0.005% bismuth or less, but with 0.01% bismuth, cracking occurred during hot rolling. After removal from the furnace at 850° C. the copper was rolled through five passes without cracking, but as it cooled through a further four passes to a temperature of approximately 600° C., many fine cracks appeared and the final rod was cold-short. The ductility was restored by quenching from 850° C. Smart and Smith suggested, from the behaviour of the material containing 0.005% bismuth, that oxygen nullified “part of the effect of bismuth” and that “part of the bismuth is removed from solution as an oxide, but the reaction does not appear to be complete and the stability of the oxide formed is questionable”.

Eborall⁵ studied the equilibrium of the system copper-bismuth-oxygen and showed that in copper-rich alloys, containing substantial amounts of bismuth and oxygen, the bismuth existed as the element at temperatures above about 800° C., but tended to form its oxide below 700° C. Voce and Hallowes¹ have shown that bismuth-embrittlement of deoxidized coppers can be explained in terms of intergranular films of elementary bismuth, and a solid solubility of bismuth in copper which increases from about 0.001% at 600° C. to about 0.01% at 800° C.

These authors also suggested that the solid solubility of bismuth in phosphorus-deoxidized copper increases rapidly at temperatures above about $700^{\circ}\text{C}.$, and that if such coppers are heated at temperatures in excess of this, quickly cooled, and then reheated below $700^{\circ}\text{C}.$, bismuth is precipitated at the grain boundaries causing embrittlement of the material.

In other work Voce and Hallows found that the maximum embrittlement of phosphorus-deoxidized coppers containing from 0.003% to 0.01% bismuth occurred after annealing the cold-rolled material at $550^{\circ}\text{C}.$, when the notched-bar value was about 5 ft.lb. If the cold-rolled strip was annealed at $750^{\circ}\text{C}.$, quenched, and re-heated to $550^{\circ}\text{C}.$, the notched-bar figure rose to about 20 ft.lb. This difference was attributed to the facility with which bismuth films formed at the grain boundaries when recrystallization accompanied bismuth precipitation. These hitherto unpublished observations are quoted because they help in the interpretation of the present test results.

III.—THE OCCURRENCE OF EMBRITTLEMENT IN TOUGH-PITCH COPPERS AND A POSSIBLE EXPLANATION.

In preliminary work it was found that when tough-pitch coppers containing 0.006% bismuth were rapidly cooled from a temperature in excess of $750^{\circ}\text{C}.$, cold rolled, and then annealed at a temperature as low as would effect recrystallization in a reasonably short time, they were liable to extreme brittleness, which was absent if annealing was carried out at a higher temperature (e.g. $550^{\circ}\text{C}.$). Full details of the occurrence of this embrittlement are given in Section IV, but for an adequate understanding of the planning of the subsequent work some indication of the theory suggested to explain the initial results is necessary.

If the solubility of bismuth in copper is not greatly affected by the presence of phosphorus and if Eborall's observation ⁵ is applicable to coppers with the lower oxygen and bismuth contents which are of more practical interest, e.g. 0.03–0.06% oxygen and up to 0.01% bismuth, such coppers should not be embrittled by the bismuth if the system is in equilibrium; at temperatures above about $800^{\circ}\text{C}.$ the bismuth would be in solid solution, while at lower temperatures, below $700^{\circ}\text{C}.$, it would occur as bismuth oxide which is regarded as harmless. If, however, the copper was first heat-treated at $800^{\circ}\text{C}.$ or higher temperatures and quenched, and then annealed below $700^{\circ}\text{C}.$, it is possible that the rate of precipitation of bismuth from solid solution might exceed the rate at which it combined with oxygen. Between 800° and $600^{\circ}\text{C}.$ the solid solubility of bismuth falls from 0.01 to 0.001%, while that of oxygen,

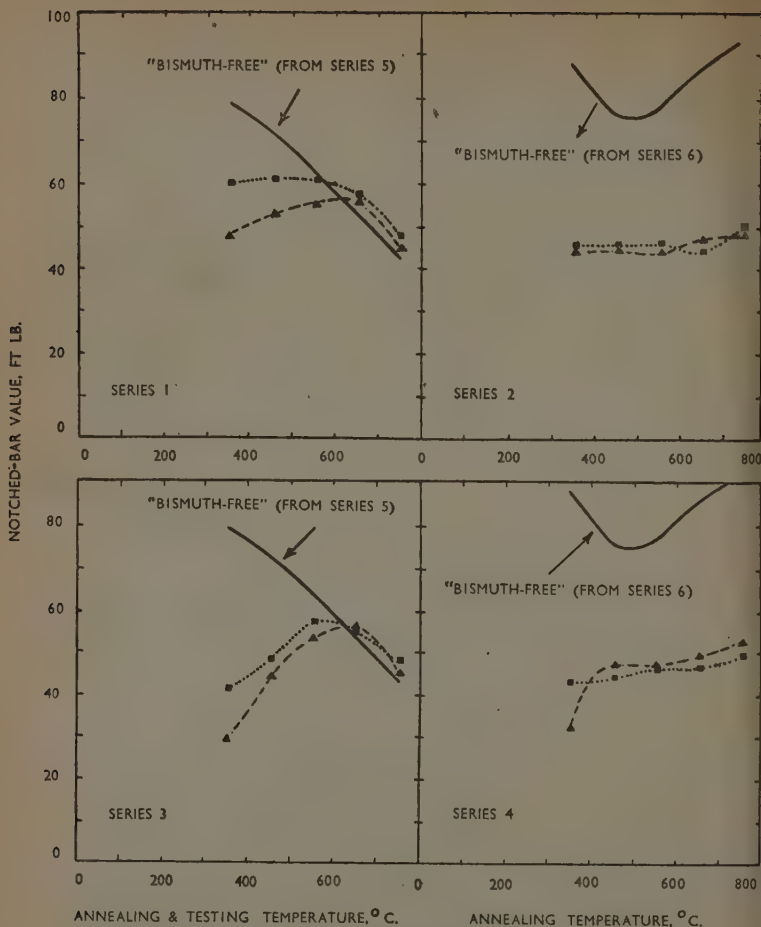


FIG. 1.—Notched-Bar Values of Tough-Pitch Coppers Containing 0.0015 and 0.0035% Bismuth.

- Series 1. Hot rolled at 800° C., rapidly air cooled, cold rolled. Fully annealed and tested at temperatures indicated without intermediate cooling.
- Series 2. Hot rolled at 800° C., rapidly air cooled, cold rolled. Fully annealed at and quenched from temperatures indicated. Tested at room temperature.
- Series 3. Annealed at 800° C., quenched, cold rolled. Fully annealed and tested at temperatures indicated without intermediate cooling.
- Series 4. Annealed at 800° C., quenched, cold rolled. Fully annealed at and quenched from temperatures indicated. Tested at room temperature.

KEY.

-■.....■..... 0.0016% Bi (NPN 1)
- ▲-----▲----- 0.0034% Bi (NPN 3)

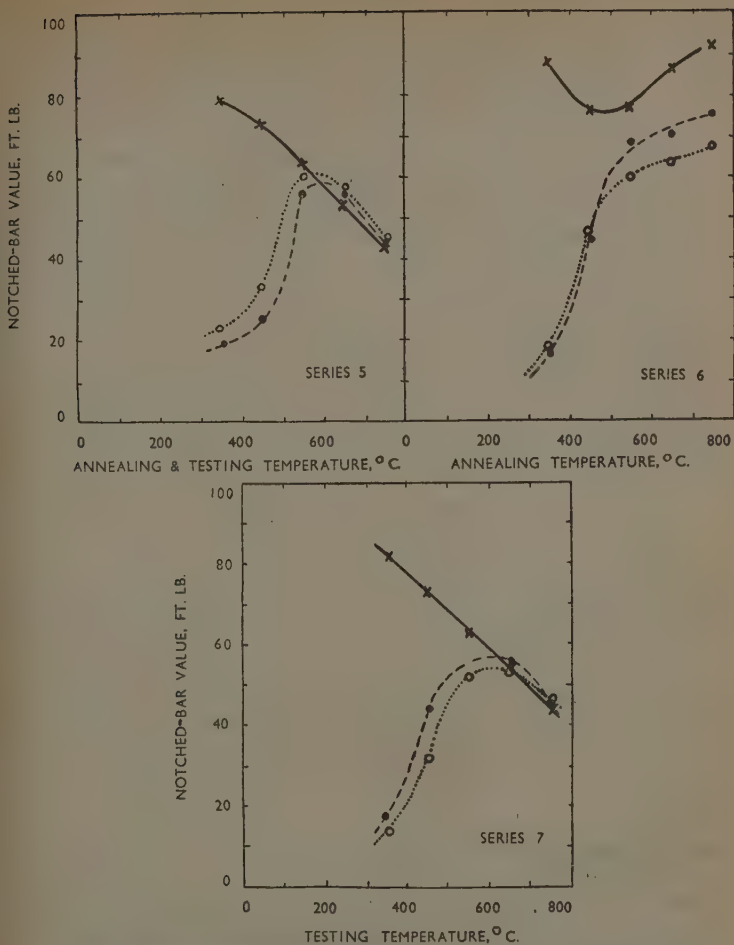


FIG. 2.—Notched-Bar Values of Tough-Pitch Coppers Containing 0.006% Bismuth.

Series 5. Hot rolled at 800° C., rapidly air cooled, cold rolled. Fully annealed and tested at temperatures indicated without intermediate cooling.

Series 6. Hot rolled at 800° C., rapidly air cooled, cold rolled. Fully annealed at and quenched from temperatures indicated. Tested at room temperature.

Series 7. Annealed 1 hr. at 800° C., quenched, cold rolled. Fully annealed and tested at temperatures indicated without intermediate cooling.

KEY.

.....○.....○.....	0.0058% Bi (LOL 1)
-----●-----●-----	0.0065% Bi (LOL 2)
————×————×————	"Bi-free" (LOL 3)

according to Phillips and Skinner,⁶ falls only from 0.0022 to 0.0019%. Whether bismuth or bismuth oxide is rejected from solution on reheating to 650° C. will depend mainly on the relative rates of diffusion of bismuth and oxygen in copper, and it is suggested that the embrittlement is due to the formation of unstable bismuth films at low temperatures. The fact that the amount of oxygen rejected from solution is only sufficient to form bismuth oxide with about 0.003% bismuth would probably favour the appearance of metallic bismuth in coppers of higher bismuth content. Metallic bismuth so formed on low-temperature annealing would, it is suggested, gradually be converted to the stable form (bismuth oxide) by increasing the temperature or the time of annealing so as to allow adequate diffusion of oxygen to occur.

If metallic bismuth is precipitated as described and causes embrittlement of tough-pitch coppers, it may be expected, by analogy with phosphorus-deoxidized coppers, that the degree of embrittlement will be greater if cold work is interposed between the solution heat-treatment and the re-heat-treatment at lower temperatures.

The present work was based on the above-stated views.

IV.—EXPERIMENTAL RESULTS.

The preparation, analyses, and grain-sizes of the materials examined and some relevant details of the notched-bar testing technique are described in Appendix I (p. 851).

Tough-pitch coppers containing 0.0001–0.006% bismuth were hot rolled at 800° C., rapidly air cooled,* and then cold rolled. Bismuth is retained in solid solution in deoxidized coppers air cooled after hot working at 800° C.,¹ but to ensure that this was so in the tough-pitch coppers examined, portions were quenched from 800° C. before cold rolling.

Coppers treated in accordance with these two schedules were reheated at temperatures from 350° to 750° C. in air for times sufficient to soften them completely, and then tested at temperature, or at room temperature after quenching. The theory predicting that these coppers might show bismuth embrittlement was confirmed by the experimental results shown in Fig. 1 (Series 1–4) and Fig. 2 (Series 5–7). The degree of embrittlement increased with the bismuth content of the coppers and was more marked when the coppers were quenched from 800° C. before cold rolling. There was no embrittlement at 550° C., the temperature at which phosphorus-deoxidized coppers show maximum brittleness, but embrittlement occurred with increasing severity as the temperature was lowered.

* See Appendix I.

To determine how far the results were affected by the interposition of cold work between high- and low-temperature heat-treatment, some of the cold rolled coppers of high bismuth content were annealed at and quenched from 900°, 800°, and 600° C., respectively, in air and then reheated to temperatures up to 750° C. for notched-bar tests without intermediate working. The results in Fig. 3 (Series 8-11) show that very little embrittlement occurred in these materials. An additional series annealed at 600° C. and air cooled before reheating to and testing at temperatures up to 750° C. gave results very similar to those shown in Series 11. The annealing times at 900° C. were varied from 1 to 8 hr. to ensure that any bismuth oxide present was dissociated and the bismuth taken into solid solution; the results were not significantly different for times of annealing of 1, 2, 4, and 8 hr., respectively, and the results in Series 8 and 9 are typical.

Fig. 4 (Series 12) shows that when the cold rolled tough-pitch coppers of high bismuth content were annealed at 550° C., no embrittlement was detected on re-heating and testing at 350°-750° C., even when cold work was interposed between the two heat-treatments.

Fig. 4 (Series 13) shows that severe embrittlement occurring in the same coppers after solution heat-treatment, cold working, and then annealing at 350° C., disappeared if the heating period at 350° C. was sufficiently long. Fig. 5 (Series 14) shows similar recovery at 450° C., after shorter heating periods, using the coppers with nominal bismuth contents of 0.0035 and 0.006%; while Series 15 (Fig. 5) shows that no embrittlement was detected in the copper of highest bismuth content (0.006%) after annealing at 550° C. for periods of time from 15 min. to 4 hr. Hardness determinations on the coppers re-heated for the shortest times in the tests of Series 13, 14, and 15 showed complete softening in all cases.

It is known that the ductility of tough-pitch copper at room temperature is lowered as the oxygen content increases, and this effect of oxygen is apparent in some of the notched-bar test results. The oxygen content of the "bismuth-free" copper was lower than that of the other materials, and it can be seen that its notched-bar values were higher than those for the bismuth-bearing materials at temperatures up to about 300° C., even though the treatment given to the coppers was such as to eliminate bismuth embrittlement (see Fig. 1, Series 2; Fig. 3, Series 8-11; Fig. 5, Series 14 and 15). A good correlation between oxygen content and notched-bar value at room temperature, 150° C., and 250° C., for coppers made virtually free from bismuth embrittlement by annealing at 550°-750° C., is shown by Fig. 6 (a) and (b).

To provide some correlation between notched-bar values and tensile

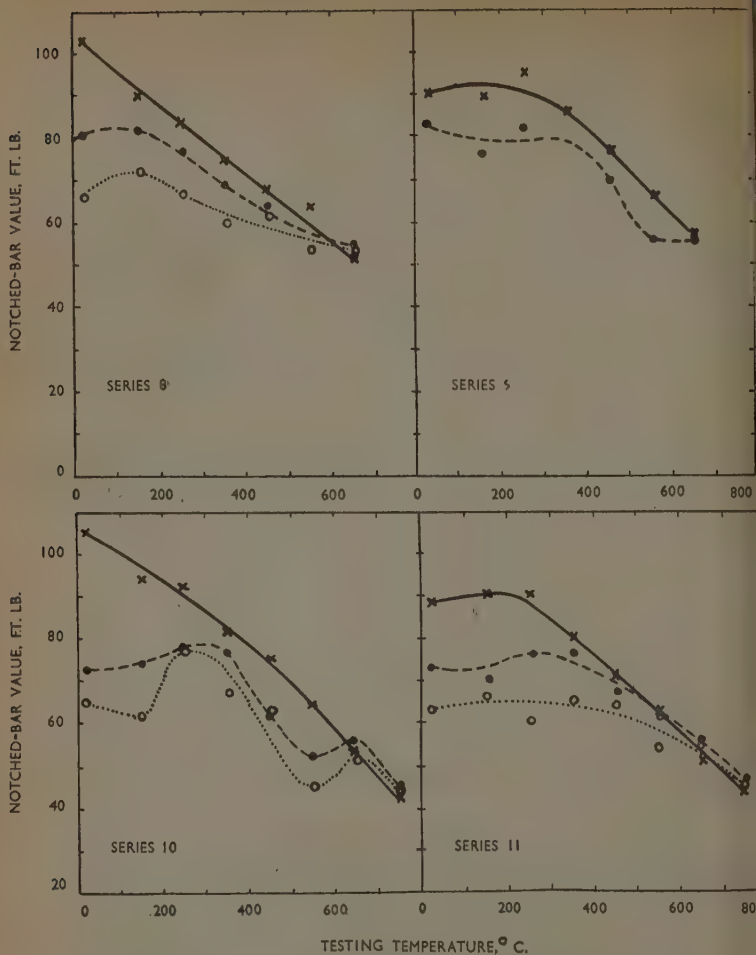


FIG. 3.—Notched-Bar Values of Tough-Pitch Coppers Containing 0.006% Bismuth.

- Series 8. Hot rolled at 800° C., rapidly air cooled, cold rolled. Annealed 1 hr. at 900° C., quenched. Reheated to test temperature.
- Series 9. Hot rolled at 800° C., rapidly air cooled, cold rolled. Annealed 4 hr. at 900° C., quenched. Reheated to test temperature.
- Series 10. Hot rolled at 800° C., rapidly air cooled, cold rolled. Annealed 1 hr. at 800° C., quenched. Reheated to test temperature.
- Series 11. Hot rolled at 800° C., rapidly air cooled, cold rolled. Annealed 1 hr. at 600° C., quenched. Reheated to test temperature.

Key as in Fig. 2.

properties, a few tensile tests were made on the "bismuth-free" material and on the copper containing 0.0065% bismuth after annealing at 350° and 450° C. for various times. The results, reported in Appendix II (p. 854), showed that even with low notched-bar values of the order of 10 ft.lb., elongation and reduction of area figures fell only to 50%; when brittleness had been removed, notched-bar values of 55-70 ft.lb. were coincident with elongation and reduction of area figures of 60-65% and 70-75%, respectively.

V.—METALLOGRAPHIC EXAMINATION.

Specimens of the coppers containing 0.006% bismuth showing embrittlement when annealed at 350° C. after cold work, and specimens of the same coppers not showing embrittlement when annealed at 550° C. after cold work (Series 5 and 6), were electrolytically polished and examined for films of the type found by Schofield and Cuckow⁷ in phosphorus-deoxidized bismuth coppers in the brittle condition. The

embrittled specimens contained numerous grain-boundary films of the same type, but there were none in the ductile specimens annealed at 550° C. Similarly, films were found in brittle specimens (Series 7), which were annealed at 800° C. and then cold worked before re-annealing

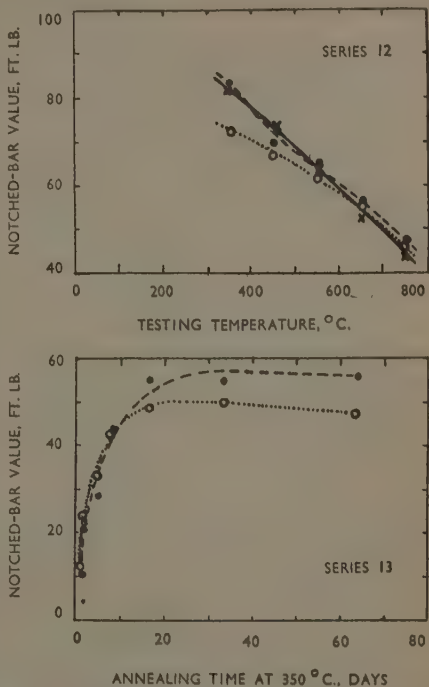


FIG. 4.—Notched-Bar Values of Tough-Pitch Coppers Containing 0.006% Bismuth.

Series 12. Annealed 1 hr. at 550° C., quenched, cold rolled. Fully annealed and tested at temperatures indicated without intermediate cooling.

Series 13. Hot rolled at 800° C., rapidly air cooled cold rolled. Annealed for prolonged periods at 350° C., quenched. Tested at room temperature.

Key as in Fig. 2.

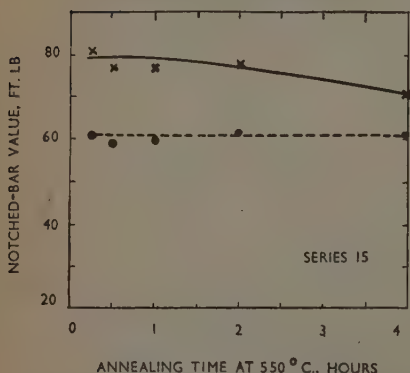
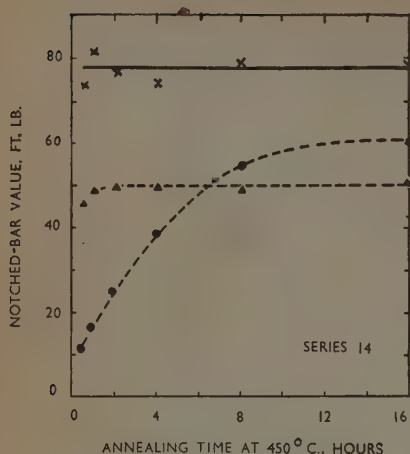


FIG. 5.—Notched-Bar Values of Tough-Pitch Coppers Containing 0.0035 and 0.006% Bismuth.

Series 14. Hot rolled at 800°C., rapidly air cooled, cold rolled. Annealed for various times at 450°C., quenched. Tested at room temperature.

Series 15. Hot rolled at 800°C., rapidly air cooled, cold rolled. Annealed for various times at 550°C., quenched. Tested at room temperature.

KEY.

---▲---●--- 0.0034% Bi (NPN 3)
 ---●---●--- 0.0065% Bi (LOL 2)
 ---×---×--- "Bi-Free" (LOL 3)

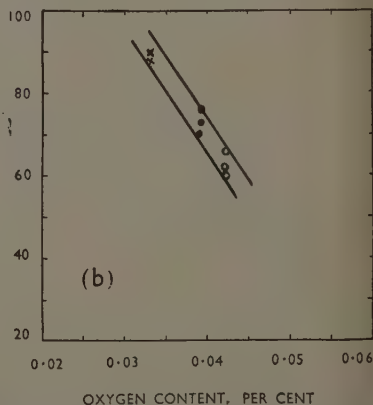
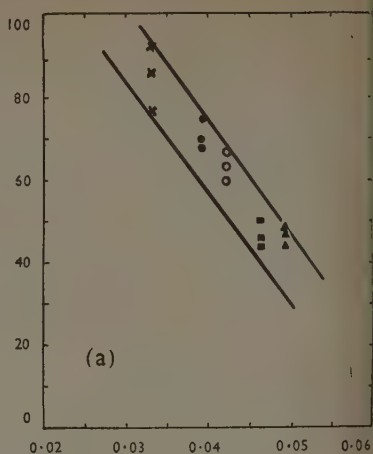


FIG. 6.—Relationship Between Notched-Bar Value and Oxygen Content of Tough-Pitch Coppers.

Fig. 6 (a). Tests from Series 2 and 6. Specimens quenched from 550°, 650°, and 750°C. Tested at room temperature.

Fig. 6 (b). Tests from Series 11. Specimens quenched from 600°C. Tested at room temperature, 150°, and 250°C.

KEY.

■ 0.0016% Bi (NPN 1) ● 0.0065% Bi (LOL 2)
 ▲ 0.0034% Bi (NPN 3) × "Bi-free" (LOL 3)
 ○ 0.0058% Bi (LOL 1)

for test purposes, while no films were seen in ductile specimens from Series 12, in which the copper was annealed at 550° C. and then cold worked before re-annealing for test.

VI.—DISCUSSION.

The test results obtained are in complete accord with the theory suggested to explain the occurrence of brittleness in bismuth-bearing tough-pitch coppers which have been rapidly cooled from a temperature of the order of 750° C. or higher, cold worked, and finally annealed at 350°–450° C. The suggestion that metallic bismuth thrown out of solution at the low temperature of recrystallization is the cause of the embrittlement, and that the brittleness disappears as this bismuth is converted to bismuth oxide, is supported by the recovery of ductility on prolonged heating at the lower temperatures.

Annealing at 500°–600° C. after cold work ensures that any precipitated bismuth is converted to bismuth oxide sufficiently rapidly to avoid embrittlement under normal manufacturing conditions; the evidence does not rule out the possibility of embrittlement after very short annealing or reheating periods at such temperatures, although it has been shown that a copper containing 0.006% bismuth is not embrittled under these conditions when annealed by re-heating for only 15 min. at 550° C.

If the bismuth-bearing copper is quenched from 800° C., and then re-annealed at lower temperatures without intermediate cold work, the embrittlement is less marked than when the low-temperature anneal causes recrystallization. The absence of intermediate cold work no doubt decreases the degree of embrittlement by discouraging the segregation of bismuth to the grain boundaries.

It is concluded that tough-pitch coppers can be embrittled by bismuth under certain conditions by a mechanism essentially similar to that causing the bismuth embrittlement of deoxidized copper. An important difference is that the temperature range of embrittlement is much lower in the tough-pitch coppers, owing to the tendency of bismuth to combine with oxygen at temperatures below 700° C. to form a relatively innocuous bismuth oxide. This combination is rapid at temperatures of the order of 550° C., and becomes progressively slower as the temperature falls; at 350° C. it has been found to take time of the order of 10 days to remove brittleness from a tough-pitch copper containing 0.006% bismuth.

VII.—PRACTICAL IMPLICATIONS.

It has already been shown ⁸ that bismuth embrittlement of phosphorus-deoxidized coppers can be avoided if cold working is preceded

by annealing at and quenching from a relatively high temperature (e.g. 750° C.).

The present work shows that annealing bismuth-bearing tough-pitch coppers at or above 800° C. followed by rapid cooling before cold work will give rise to embrittlement if the material is subsequently re-heated to temperatures of the order of 350°–450° C., either for further working or in service. Similarly, hot working at temperatures of the order of 800° C. or over will induce embrittlement if the copper is rapidly cooled after hot working, then cold worked and reheated to between 350° and 450° C. The brittleness is slowly removed as the heating period in this lower temperature range is extended, and to avoid embrittlement tough-pitch coppers containing bismuth should be soaked at a temperature between 500° and 600° C., before proceeding with cold working. The rate of cooling after this heat-treatment is immaterial.

It is also possible that tough-pitch coppers containing bismuth and hot worked over a range of temperatures falling from 800° C. or above, may enter a brittle range in the region from about 500° to 350° C. and, if this difficulty is encountered, the remedy is to reheat the materials more frequently, to maintain a higher working temperature, and finally to soak them at 500°–600° C. before proceeding with any subsequent cold work.

With a normal grain-size the embrittlement discussed above may be severe with bismuth contents exceeding about 0.0035%; with lower bismuth contents it is unlikely to have much practical significance.

ACKNOWLEDGEMENTS.

The author wishes to thank the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish this work, which is part of a general investigation of the effects of bismuth, selenium, and tellurium in copper.

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APPENDIX I.

1. *Materials Used.*

Two 300-lb. tough-pitch cakes (0.006% bismuth) and two 100-lb. tough-pitch billets (0.0015% and 0.0035% bismuth, respectively) were vertically cast * from fire-refined charges, mainly of high-conductivity electrolytic-copper scrap, after appropriate additions of bismuth. Another cake, vertically cast from remelted "bismuth-free" O.R.C. electro-ingots, provided a standard of reference. Analyses are given in Table I, from which it will be seen that the control material (mark

TABLE I.—*Analyses of Tough-Pitch Coppers.*

Mark	LOL3	NPN1	NPN3	LOL1	LOL2
<i>Chemical Analysis:</i>					
Bismuth, % . . .	<0.0001†	0.0016	0.0034	0.0058	0.0065
Oxygen, % . . .	0.033	0.046	0.049	0.042	0.039
Copper, % . . .	99.96	99.91	99.91	99.93	99.94
Sulphur, % . . .	0.0029	0.004	0.004	0.0033	0.004
Selenium, %	<0.001	<0.001	<0.001	<0.002
Tellurium, %	<0.001	<0.001	<0.002	<0.001
<i>Spectrographic Analysis:</i>					
Iron, % . . .	0.0002	0.0005	0.0002	0.0005	0.0005
Lead, % . . .	<0.0003	0.0005	0.0005	0.0004	0.0004
Manganese, % . . .	<0.001	<0.001	<0.001	~0.001	~0.001
Nickel, % . . .	0.0003	0.001	0.0006	0.001	0.001
Silver, % . . .	0.001	0.004	0.004	0.004	0.004
Tin, % . . .	0.0005	0.0005	0.0005	0.0005	0.0005
Silicon, % . . .	<0.008	<0.008	<0.008	<0.008	<0.008
Antimony, % . . .	<0.0002	0.001	0.001	<0.0002	<0.0002
Arsenic, % . . .	<0.002	0.002	0.002	<0.002	<0.002
Cobalt, % . . .	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Zinc, % . . .	0.001	0.004	0.004	0.001	0.001
Tellurium, % . . .	<0.004	<0.004	<0.004	<0.004	<0.004

† No bismuth addition.

LOL3) contained only 0.001% silver compared with 0.004% in the bismuth-bearing coppers; some of the results reported later (Table III) indicate that the recrystallization temperature of the coppers with the higher silver content was raised to some extent.

The cakes of high bismuth content (0.006%) were hot rolled at about 800° C. from 4 in. to 0.75 in. thickness, rapidly air cooled (i.e. cooled individually, without stacking), and then cold rolled to 0.4 in. in ten passes, without intermediate annealing. Additional cold work required

* Through the courtesy of Messrs. Thomas Bolton & Sons Ltd.

on these materials to enable the tests in Series 8 and 9 to be made, consisted of cold rolling in the laboratory.

The billets were similarly hot rolled at about 800° C. to 0.75 in. thickness and halves of the resulting strips were rapidly air cooled and then cold rolled to 0.4 in. The other halves of the 0.75 in. strips were re-heated to 800° C., quenched, and then cold rolled to 0.4 in. thickness.

2. Grain-Sizes.

Portions of the notched-bar specimens used for the tests in Series 1, 3, 5, and 7 were examined for grain-size after annealing and testing at temperatures of 350°, 550°, and 750° C. One of the coppers selected was "bismuth-free" (LOL3), the others containing 0.0016, 0.0034, and 0.0065% bismuth (NPN1, NPN3, and LOL2, respectively).

At any of the annealing temperatures chosen, the "bismuth-free" copper was slightly more coarse-grained than the other materials, although there were no perceptible variations in grain-size as the bismuth content was increased from 0.0016 to 0.0065%. The grain-sizes were governed by the final annealing treatment and were independent of the earlier histories of the materials. Representative figures are given in Table II.

TABLE II.—*Grain-Sizes of Tough-Pitch Coppers.*

Annealing Temp., ° C.	Grain Size ($\sqrt{\text{Area of Average Grain}}$, mm.)			
	Coppers Containing 0.0016–0.0065% Bismuth		"Bismuth-Free" Copper	
	Range	Mean	Range	Mean
350°	0.012–0.017	0.015	0.015–0.017	0.016
550°	0.012–0.016	0.014	0.019–0.022	0.021
750°	0.018–0.022	0.020	0.026–0.030	0.028

3. Experimental Details.

Specimens, 6 × 1 × 1 cm., were cut from the rolled strip, parallel to the rolling direction, for notched-bar tests on an Izod machine with beam specimens machined with a standard Izod notch. For the tests at elevated temperatures, the specimens were transferred to the anvil of the machine and broken within 2 sec. of leaving the furnace.

When cold work preceded annealing for testing, the annealing times were adjusted to give fully softened specimens, and further annealing did not lower the hardness of the material. Table III shows a few

typical results, from which the curves for Series 5 (Fig. 2) were plotted. The annealing times shown in Table III for 450° C. and higher temperatures were used in all tests employing cold-worked specimens; the annealing time at 350° C. was 24 hr., and since it proved impracticable to soften the bismuth-bearing materials completely by annealing at 250° C., no tests were made on materials originally cold rolled and then annealed at this temperature.

TABLE III.—*Notched-Bar and Hardness Values of Bismuth-Bearing and " Bismuth-Free " Coppers.*

Notched-bar specimens annealed as indicated and tested at the annealing temperature without intermediate cooling.

Condition of Material	0.0058% Bismuth (LOL1)	0.0065% Bismuth (LOL2)		" Bismuth-Free " (LOL3)	
	Notched-Bar Value, ft.lb.	Notched-Bar Value, ft.lb.	Hardness, D.P.N., at Room Temperature	Notched-Bar Value, ft.lb.	Hardness, D.P.N., at Room Temperature
As rolled	20	22	111	38	109
16 hr. at 250° C. . .	25	28	111	86	56
45 days at 250° C..	22	18	78	87	44
2 hr. at 350° C. . .	19	13	71	84	53
24 hr. at 350° C. . .	23	19	48	79	43
2 hr. at 450° C. . .	33	25	49	73	47
1 hr. at 550° C. . .	60	56	47	63	44
1 hr. at 650° C. . .	57	57	46	53	44
30 min. at 750° C..	45	44	45	43	44

In the tests of Series 8, 9, 10, and 11, in which the specimens were reheated to the test temperature after initial annealing, the specimens were held at the reheating temperature for at least $\frac{1}{2}$ hr. before testing.

APPENDIX II.

Tensile Tests.

Duplicate tensile specimens, cut longitudinally from the rolled strips of both the "bismuth-free" material and the copper containing 0.0065% bismuth, and with a parallel portion 1.16 in. long \times 0.282 in. dia. were annealed in air at 350° C. for 1, 4, and 16 days, and at 450° C. for 30 min., 4, and 16 hr., respectively, and quenched. The annealing times were chosen on the basis of the notched-bar results in Series 13 and 14 (Figs. 4 and 5) and the test results (Table IV) provide a comparison between tensile and notched-bar values under similar conditions of heat-treatment.

TABLE IV.—*Tensile Properties and Notched-Bar Values of Tough-Pitch Coppers.*

Mark	Composition, %		Annealing Treatment		Tensile Strength, tons/in. ²	Elongation on 1 in., %	Reduction of Area, %	Notched-Bar Value, ft. lb.
	Bismuth	Oxygen	Temperature, ° C.	Time				
LOL3	<0.0001	0.033	350°	1 day	14.2	65	76	57 *
			350°	4 days	14.4	63	76	63 *
			350°	16 days	14.4	61	74	73 *
LOL2	0.0065	0.039	350°	1 day	14.6	51	50	11
			350°	4 days	14.6	56	57	29
			350°	16 days	14.8	59	72	55
LOL3	<0.0001	0.033	450°	$\frac{1}{2}$ hr.	14.3	64	75	74
			450°	4 hr.	14.3	63	74	74
			450°	16 hr.	14.5	65	74	63
LOL2	0.0065	0.039	450°	$\frac{1}{2}$ hr.	14.5	52	53	12
			450°	4 hr.	14.7	61	70	39
			450°	16 hr.	14.7	62	71	61

* Unusually wide scatter of results; not plotted in Series 13 (Fig. 4).

NOTE ON A PARTICULAR TYPE OF COLD WORKING OF GRAINS OF α -BRASS BY ROLLING.*

By Ing. J. SCHOofs,† Ingénieur A.I.Lg.

SYNOPSIS.

By the use of a special electrolytic polishing and etching procedure devised by the author, a new metallographic feature has been revealed in a certain number of crystals of an α -brass that had received a particular annealing and cold-working treatment. This feature takes the form of a series of bright, narrow bands across the grains, which may on occasion extend into adjacent grains. At the present stage of development of X-ray diffraction technique, the precise nature of these bands cannot be determined. However, two possible explanations of their formation are advanced and discussed; it seems most likely that the bands are due to mechanical twinning.

I.—THE NATURE OF THE PHENOMENON.

THEORIES of the plastic deformation of polycrystalline metals suppose that those crystallizing, as α -brass does, in the face-centred cubic lattice deform by slip along the (111) planes, and in these metals the formation of mechanical twins is regarded as quite exceptional.

The object of the present note is to show that some mechanical twins appear to be formed during the rolling of α -brass in crystals that fulfil certain conditions.

The sample examined consisted of a sheet of brass, containing 72% copper, annealed in such a way as to produce a grain-size of 0.11 mm., as measured by the A.S.T.M. method. The sheet was then given a reduction in thickness of 13% at a single pass. Some specimens of the rolled sheet were taken for micro-examination and prepared by electrolytic polishing and etching by the short-circuit procedure described elsewhere.¹

All the photomicrographs reproduced (Figs. 1-4, Plates CX and CXI) were taken from the surface of the sheet, without emerying, and thus represent the actual surface skin.

Certain grains reveal the presence of bright, narrow bands, divided longitudinally by a fine line and generally ending in a point, which may lie either in the same grain (Fig. 1) or in the adjacent grain (Fig. 2).

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In some cases there is no such point (band at the bottom of Fig. 2), the bright band retaining the same width up to the grain boundary.

In addition to the line along the axis of each band, which invariably ends at the grain boundary, there is always found between each pair of bands a fine line which stops at the grain boundary when the points of the bands do so or when the bands have no point, and continues, generally slightly deflected, into the adjacent grain when the points of the bands also extend into that grain (Fig. 2).

The bands and the lines between them are always straight and parallel provided the rolling reduction is not too great. Both the bands and the lines extend from one grain boundary to the opposite boundary ; or, when a band ends in the middle of a grain, the line on one side or

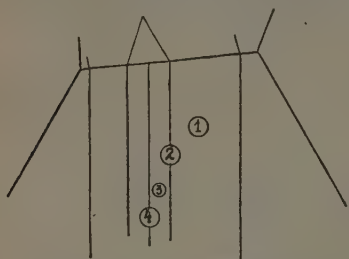


FIG. 5.—Diagram of a Band, Showing Points at which X-Ray Diffraction Diagrams will be Required, if the Nature of the Band is to be Resolved.

the other of it also stops (Figs. 3 and 4). With greater degrees of reduction, the bands deform and the axial line becomes much less distinct (Fig. 4).

The direction of the bands is perpendicular to the rolling direction or departs from it by an angle that never exceeds 20° .

The grains exhibiting the phenomenon are not numerous, and in a particular brass appear only under certain definite conditions of reduction and preliminary annealing. The explanation of the phenomenon would be facilitated were it possible to examine by X-rays spots (circles marked 1, 2, 3, 4 in Fig. 5) of a maximum diameter of $2\text{--}3\ \mu$. As such an examination cannot be carried out at the present stage of development of the X-ray technique, it is possible only to theorize about the formation of the bands.

II.—THEORETICAL EXPLANATION.

Two explanations of the phenomenon can be advanced ; both have arguments for and against.

Figs. 1-4 (Plates CX and CXI) show without any doubt, in the author's opinion, that the crystals in the annealed state are twinned. The formation of twins on annealing α -brass is in fact very common, and it is true to say that in an annealed α -brass the great majority of the crystals are twinned. The straight and parallel character of the bands and the lines between them supports this view.

Grains of α -Brass Exhibiting Bright Bands.



FIG. 1.—Bands Having Points Lying Within the Same Grain. $\times 1000$.

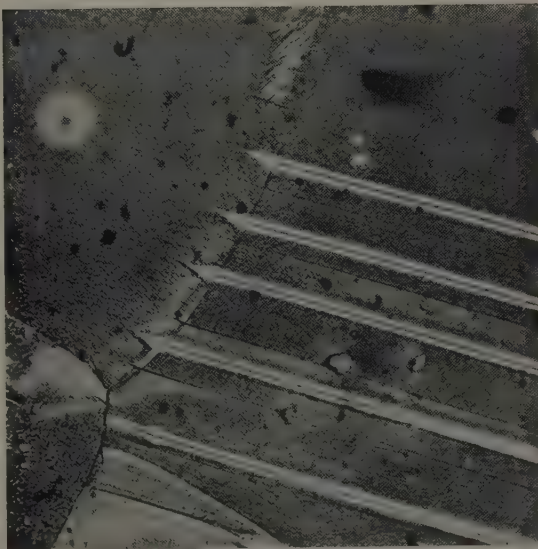


FIG. 2.—Bands Having Points Lying in the Adjacent Grain. $\times 500$.

Grains of α -Brass Exhibiting Bright Bands.



FIG. 3.—Bands Without Points and Band Ending in the Middle of a Grain. $\times 500$.



FIG. 4.—More Heavily Worked Grain, Showing Distortion of the Bands. $\times 500$.

The fact that the grain as a whole, apart from the bands, has a uniform colour shows that the twinned parts have the same orientation with respect to the plane of the sheet. The twinning planes are therefore perpendicular to the plane of the sheet and also, as already stated, perpendicular to the rolling direction. The grains in question must therefore lie as shown in Fig. 6, and a section perpendicular to the plane of the sheet and parallel to the rolling direction will thus be a (110) plane throughout the grain. Fig. 7 represents such a plane before rolling, with the trace of a twinning plane P (where a band will be produced), as well as traces of (111) slip planes before rolling (fine continuous lines) and (100) planes (fine broken lines).

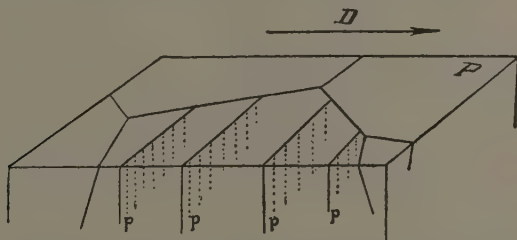
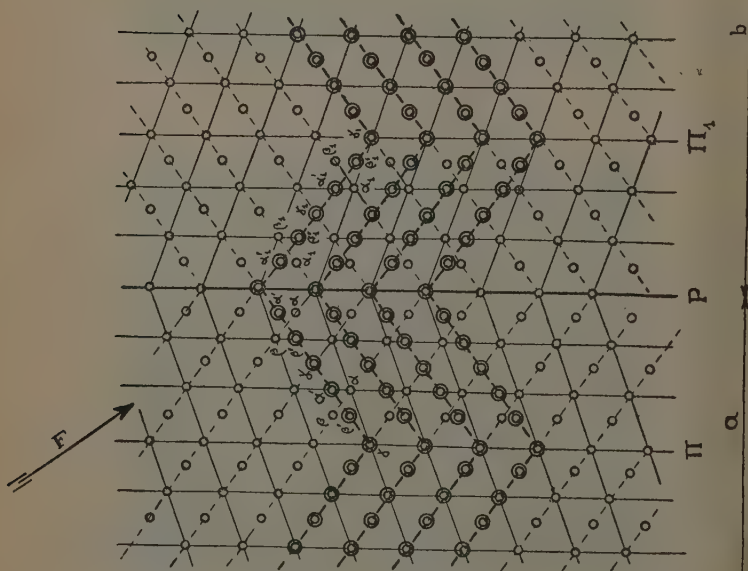
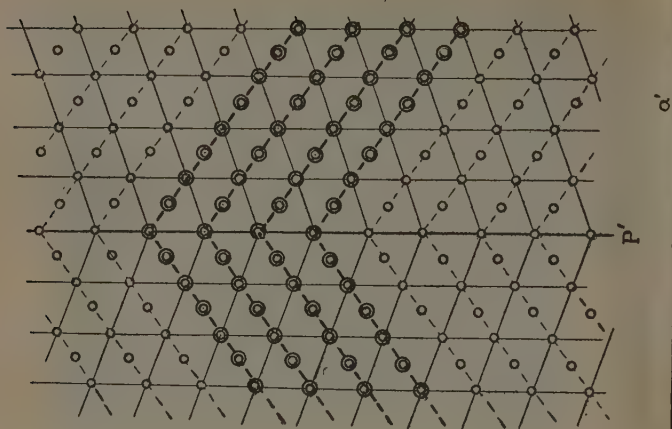


FIG. 6.—Disposition of Twinned Crystals in Rolled Sheet.

D = rolling direction.
 P = rolling plane and plane of sheet.
 p = twinning planes.

Suppose that in the course of rolling the sheet moves from right to left, or, what amounts to the same thing, the rolling force in the sheet moves from left to right. Near the surface this rolling force F lies at an angle to the plane of rolling and in the opposite direction to the movement of the sheet. The angle varies from the surface of the sheet to the centre, where, by reason of symmetry, the force is perpendicular to the plane of the sheet.

Consider the situation at the moment when the rolling force is applied to the mid-point of the width of the twinned part a (Fig. 7) and hence at a microscopically great distance from the twinning plane P . In this position the slip planes are unfavourably orientated in relation to the force F and the grain deforms elastically, finally compressing adjoining grains which are more favourably orientated for slip. After the force has passed by, the part a will resume its former shape and will not show any signs of cold working, at any rate for sufficiently small values of F , i.e. for small rolling reductions.



On the other hand, when F is applied to the part b at microscopically great distances from the twinning planes which bound it, the slip planes are more favourably orientated and b deforms by slipping. As F approaches the twinning plane P' it is preceded by slipping, which reaches P' before F does and can, at least in part, be transmitted to the part a' on the far side of the twinning plane P' , provided that the angle formed by the directions of slip in the twinned parts is in the region of 180° . Hence along the planes P' nothing of significance can occur except a little cold working. Traces of the planes P' in the plane of the photomicrographs (Figs. 1-4) appear as fine lines between the bands.

The phenomena that can occur in the immediate vicinity of the twinning planes P will now be considered.

1. *First Hypothesis : Formation of Mechanical Twins.*

According to this hypothesis, when F is applied to the part a (Fig. 7), and affects the region of the grain immediately adjacent to the twinning plane P , the latter forms a discontinuity in the lattice and a barrier to the elastic deformation of a . Under these conditions F exerts a turning moment on a , with the result that α and β atoms (Fig. 7) are displaced to the positions α' and β' , γ atoms remaining stationary. A twin is thus formed on the two sides of a new twinning plane π , the (100) planes of the new twinned region being orientated as shown by the thick broken lines in Fig. 7.

When F reaches the portion b immediately to the right of the twinning plane P , slip cannot occur in the immediate vicinity of P and F again gives rise to a turning moment, this time of opposite sign to the first one. A mechanical twin is again formed as the result of displacement of atoms α_1 and β_1 to positions α_1' and β_1' , γ_1 atoms remaining stationary. The new twinning plane in this case is π_1 .

Thus, by this hypothesis, a mechanical twin is formed on each side of the initial twinning plane P , and it is these mechanical twins that appear in the photomicrographs as bright bands. The axial line in each band is the trace of the initial twinning plane P , while the traces of the planes of mechanical twinning π and π_1 form the edges of the band.

2. *Second Hypothesis : Intense Local Cold Working.*

The formation of the bands could equally well be explained by supposing that when the rolling force F approaches the twinning plane P , the latter forms a barrier to elastic deformation and results in a concentration of stress leading to a very high degree of cold work. The

same would occur on the other side of P , where resistance to slipping would cause cold working by curvature of the planes or fragmentation of the lattice. On this theory, it is the heavily cold-worked zones on both sides of P that cause the bands to appear.

3. *Discussion of the Two Hypotheses.*

By reference to Figs. 1-3 (Plates CX and CXI) it will be seen that, for relatively light rolling passes (13% reduction in thickness), the axial lines in the bands have a photographic density greater than that of the lines between the bands. But on the assumption that the bands are a manifestation of intense local cold working, the opposite would be expected; indeed the disturbances set up in the lattice would tend to reduce the difference in orientation of the twinned regions immediately on each side of the twinning plane P and the latter would diminish in intensity.

Moreover, the parallelism and relative sharpness of the edges of the majority of the bands are equally difficult to explain on the basis of the second hypothesis; actually the cold working of metallic crystals always gives rise (mechanical twinning apart) to irregular and ill-defined zones in which a more or less variable concentration of slip lines is observed. On the other hand, cold working by mechanical twinning gives rise to the formation of zones of markedly different metallographic appearance, separated from one another by clear-cut rectilinear boundaries. The manifestation of this phenomenon corresponds, therefore, to the description of the bands that has been given above.

The formation of the points at the end of the bands, either inside or outside the grain, can be explained by both hypotheses. When they are within the grain, the points delimit the zone which, being near to the grain boundary and influenced by the adjacent unfavourably orientated grain, could not undergo either the twinning or the cold working of the band. When the point of the band lies in the neighbouring grain, however, it is an indication that the latter was sufficiently favourably orientated to be deformed by the stresses set up by twinning or cold work. It is only to be expected that as the stresses diminish with the distance from the boundary, the deformed zone in the adjoining grain becomes narrower and narrower. It is equally to be expected, and for the same reason, that the line between the bands will be prolonged into the adjacent grain. Further, in this case, a deformed zone appears along the boundary in front of the parts of the initial twin which were the site of slip; this is clearly visible in Fig. 2 (Plate CX) and also in Fig. 3 (Plate CXI), which shows a grain consisting of two

twinned parts that themselves admit of twinning along another (111) plane.

If the formation of the bands were due to intense cold working along the twinning planes, the width of the bands would increase with the amount of cold work. In practice this is not so, a reduction in thickness of 25% instead of 13% leading to no increase in band width.

It is also observed that, as the rolling reduction increases, the edges of the band become sharper, while the axial line of the band diminishes in intensity to such a degree as to be scarcely visible in some parts of the band (Fig. 4, Plate CXI).

The first of these two observations is difficult to explain by either hypothesis; the second observation can be explained on the basis of both hypotheses by supposing that successive passes have resulted in fragmentation of the lattice in the neighbourhood of the initial twinning plane, a fragmentation which has the effect of tending to destroy the initial symmetry with reference to the axis of the band.

III.—CONCLUSIONS.

It will be seen, therefore, that the phenomenon of band formation gives rise to a number of characteristic features which can be explained in part by the hypothesis of mechanical twinning and in part by that of intense local cold working, and that it is impossible to eliminate with certainty either of the two hypotheses. The explanation on the basis of mechanical twinning appears, however, to be the more satisfactory, and this is the one which it is proposed to adopt pending the development of a method of investigation that will enable the question to be settled conclusively.

It remains to be explained why the phenomenon has not been observed previously. This can scarcely be regarded as surprising in view of the fact that, for the bands to be revealed in the present work, it was necessary not only for the orientation of the twinned grains in the sheet to be closely controlled (in the specimens examined only one grain in a thousand has been found to exhibit the phenomenon), but a special method of etching was required to show them up. Chemical etching even after electrolytic polishing is too drastic.

Nor is examination of the bands by X-ray diffraction methods possible in the present stage of the technique, since if the bands are caused by mechanical twinning, the phenomenon would only modify the arrangement of the twinned parts of a grain and this would not show on the diffraction diagram; or if they are caused by local cold working more intense than the average, the volume of material involved is too small to affect the X-ray diagram.

ACKNOWLEDGEMENT.

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1. M. Jaroszewicz-Bortnowski and J. Schoofs, *Rev. univ. Mines*, 1949, [ix], 5, (5), 170.

A RAPID METHOD FOR ESTIMATING THE 1186 HYDROGEN CONTENT OF WROUGHT ALUMINIUM ALLOYS.*

By A. J. SWAIN,† M.A., STUDENT MEMBER.

(Communication from the British Non-Ferrous Metals Research Association.)

SYNOPSIS.

A quantitative correlation is found between the voids formed in specimens of aluminium-7%-magnesium alloy sheet when immersed in molten potassium dichromate at 580° C. for 10 min., and the hydrogen content of the material determined by the vacuum-extraction method. This forms the basis of a simple and rapid method for estimating the hydrogen content of a wrought sample of this alloy to an accuracy, in the range investigated, of approximately ± 0.10 c.c. at N.T.P./100 g.

It is suggested that the use of this method could be extended to other wrought aluminium alloys having comparatively wide freezing ranges.

The method is not likely to prove suitable for use with cast materials.

I.—INTRODUCTION.

THE hydrogen content of wrought aluminium alloys is of considerable importance, especially when the alloys are to be used for welding.^{1, 2} The method of vacuum extraction for its determination is accurate and well established, but requires special apparatus and some skill. Moreover, it is not particularly rapid, especially for alloys with a volatile and reactive major constituent, such as magnesium, for with such alloys it may be necessary to clean the apparatus between single determinations. There is, therefore, considerable scope for a simple and rapid method for estimating the hydrogen content, which would not necessarily be of high accuracy but would be capable of application in any metallurgical laboratory.

The need for such a test was felt when it became necessary to determine the hydrogen content of a large number of samples of aluminium-7%-magnesium alloy sheet. The method described was, therefore, evolved.

Although, for the purpose immediately in view it was only necessary to standardize the method for the 7%-magnesium alloy, there is no apparent reason why its use should not be extended to other aluminium alloys having comparatively large freezing ranges, such as the Duralumin, zinc-magnesium-copper, or 3½%-magnesium types.

It is well known that the gas in aluminium alloys consists almost

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entirely of hydrogen, which is frequently present in amounts considerably in excess of the equilibrium solid-solubility value at atmospheric pressure. The formation of blisters is attributed to the association of hydrogen at suitable surfaces within the metal to give molecular hydrogen, at pressures which may be as high as several hundred atmospheres before expansion occurs and the blisters develop. That this takes place readily when the alloy is in the solidus-liquidus range is evident from the facility with which aluminium-7%-magnesium alloy sheet, of rather high hydrogen content, blisters during welding in those regions which have been partially melted.

It was thought that if specimens of the alloy could be heated to a suitable temperature in the solidus-liquidus range, under conditions where there would be little or no absorption or loss of hydrogen at the surface, the amount of blistering would be quantitatively related to the hydrogen content of the material. Immersion in a bath of molten potassium dichromate was found to fulfil these conditions satisfactorily owing, it is thought, to the formation of a heavy brownish surface film which probably prevents the passage of hydrogen.

II.—EXPERIMENTAL PROCEDURE FOR ALUMINIUM-7%-MAGNESIUM ALLOY.

Specimens weighing approximately 2.5 g. are used. This weight has been found convenient for density measurements, and corresponds to $\frac{3}{4}$ -in.-square specimens of 10-S.W.G. sheet, which is the form of material for which the test has been most used.

The density of the specimens is determined before and after salt-bath treatment from the weights in air and benzene by the usual method. Weighings are made on a chemical balance to an accuracy of better than ± 0.0002 g., which gives a possible error of ± 0.001 g./c.c. in a density of approximately 2.6 g./c.c., for specimens of the size quoted above.

The quantitative measure of porosity used is the volume of cavities per unit volume of *sound* metal in the blistered specimens, and will be referred to as the cavity: metal ratio. This is calculated from the density values before and after blistering.* The weighing errors quoted above are equivalent to a possible error of less than ± 0.001 in the cavity: metal ratio.

* Cavity: metal ratio (volume of cavities: unit volume of sound metal)

$$= \frac{\text{initial density} - \text{final density}}{\text{final density}}$$

This quantity is not equivalent to the conventional measure, “% voids”; the latter relates the volume of cavities to the total volume of the sample and not, as required here, to the volume of sound metal.

The procedure for salt-bath treatment for the 7%-magnesium alloy is as follows. The hydrated oxide normally present on the surface of the specimens is removed by scratch-brushing immediately before immersion. The specimens are suspended vertically from a horizontal wire (e.g. Inconel) and immersed to a depth of approximately 5 in. in a bath of molten potassium dichromate maintained at $580 \pm 5^\circ \text{C}$. After 10 min. the specimens are removed from the bath and allowed to cool in air. The dichromate adhering to them is removed in boiling water before the final density determination.

III.—STANDARDIZATION OF METHOD FOR ALUMINIUM-7%-MAGNESIUM ALLOY.

The method was standardized for 10-S.W.G. sheet by testing twelve specimens chosen at random from each of six materials whose hydrogen contents (Table I) had been determined by vacuum extraction. To obtain a proper estimate of the reproducibility of a single test the specimens were tested in batches of two or four, each containing only one specimen of any one material.

TABLE I.—*Hydrogen Contents Determined by Vacuum Extraction.*

Material	Hydrogen Content, c.c. at N.T.P./100 g.
A	0.01
	0.00
	Average 0.00
B	0.01
	0.01
	0.10
	Average 0.04
C	0.14
D	0.19
	0.19
	Average 0.19
E	0.58
	0.58
	Average 0.58
F	0.86
	0.87
	Average 0.86

TABLE II.—*Results of Tests on Aluminium-7%-Magnesium Alloy at 580° C. for 10 min.*

Material	Density, g./c.c.		Cavity: Metal Ratio	Material	Density, g./c.c.		Cavity: Metal Ratio
	Before Test	After Test			Before Test	After Test	
A	2.610	2.610	0.00×10^{-2}	D	2.609	2.587	0.85×10^{-2}
	2.615	2.610	0.19 "		2.608	2.583	0.97 "
	2.614	2.612	0.08 "		2.608	2.584	0.95 "
	2.616	2.610	0.23 "		2.609	2.584	0.97 "
	2.615	2.614	0.04 "		2.606	2.590	0.62 "
	2.616	2.611	0.19 "		2.611	2.592	0.73 "
	2.615	2.610	0.19 "		2.610	2.593	0.65 "
	2.616	2.612	0.15 "		2.610	2.591	0.73 "
	2.615	2.611	0.15 "		2.610	2.592	0.69 "
	2.611	2.612	-0.04 "		2.610	2.594	0.62 "
	2.614	2.616	-0.08 "		2.612	2.590	0.85 "
	2.617	2.614	0.11 "		2.610	2.595	0.58 "
Average	2.615	2.612	0.10×10^{-2}	Average	2.609	2.589	0.77×10^{-2}
Standard deviation $\pm 0.10 \times 10^{-2}$				Standard deviation $\pm 0.15 \times 10^{-2}$			
B	2.594	2.576	0.70×10^{-2}	E	2.600	2.509	3.63×10^{-2}
	2.593	2.577	0.62 "		2.602	2.491	4.46 "
	2.594	2.576	0.70 "		2.601	2.503	3.92 "
	2.595	2.579	0.62 "		2.601	2.506	3.79 "
	2.595	2.577	0.70 "		2.600	2.509	3.63 "
	2.596	2.578	0.70 "		2.600	2.501	3.96 "
	2.595	2.579	0.62 "		2.599	2.510	3.54 "
	2.596	2.581	0.58 "		2.600	2.508	3.67 "
	2.596	2.580	0.62 "		2.601	2.508	3.71 "
	2.593	2.579	0.54 "		2.601	2.509	3.67 "
	2.593	2.578	0.58 "		2.601	2.502	3.96 "
	2.597	2.579	0.70 "		2.602	2.521	3.21 "
Average	2.595	2.578	0.64×10^{-2}	Average	2.601	2.506	3.76×10^{-2}
Standard deviation $\pm 0.06 \times 10^{-2}$				Standard deviation $\pm 0.30 \times 10^{-2}$			
C	2.609	2.600	0.35×10^{-2}	F	2.617	2.468	6.04×10^{-2}
	2.613	2.603	0.38 "		2.616	2.464	6.17 "
	2.613	2.598	0.58 "		2.615	2.462	6.21 "
	2.612	2.601	0.42 "		2.619	2.451	6.85 "
	2.610	2.597	0.50 "		2.615	2.459	6.34 "
	2.603	2.590	0.50 "		2.617	2.472	5.87 "
	2.614	2.603	0.42 "		2.615	2.451	6.69 "
	2.613	2.603	0.38 "		2.617	2.465	6.17 "
	2.613	2.603	0.38 "		2.616	2.466	6.08 "
	2.612	2.601	0.42 "		2.616	2.459	6.38 "
	2.612	2.602	0.38 "		2.618	2.471	5.95 "
	2.610	2.594	0.62 "		2.618	2.474	5.82 "
Average	2.611	2.600	0.44×10^{-2}	Average	2.616	2.463	6.21×10^{-2}
Standard deviation $\pm 0.09 \times 10^{-2}$				Standard deviation $\pm 0.31 \times 10^{-2}$			

TABLE III.

Material	Cavity : Metal Ratio	Volume of Hydrogen Required to Fill Voids at 580° C. and 1 Atmosphere Pressure, c.c. at N.T.P./100 g.	Hydrogen Content by Vacuum Extraction, c.c. at N.T.P./100 g.
A	0.10×10^{-2}	0.01	0.00
B	0.64×10^{-2}	0.08	0.04
C	0.44×10^{-2}	0.05	0.14
D	0.77×10^{-2}	0.10	0.19
E	3.76×10^{-2}	0.46	0.58
F	6.21×10^{-2}	0.76	0.86

The results of this experiment are shown in Table II. Table III shows the volume of hydrogen required to fill the voids at 580° C. and 1 atmosphere pressure, calculated from the average figure for the cavity : metal ratio, compared with the hydrogen content determined by the vacuum-extraction method for each material. The results are shown graphically in Fig. 1.

The points representing the mean values for the cavities fall on a straight line within close limits when plotted against the hydrogen content, except for material A, which is practically gas-free and thus could not develop significant cavities, and for material B. The latter material is assumed to be anomalous (see, however, Table I, which indicates that it may

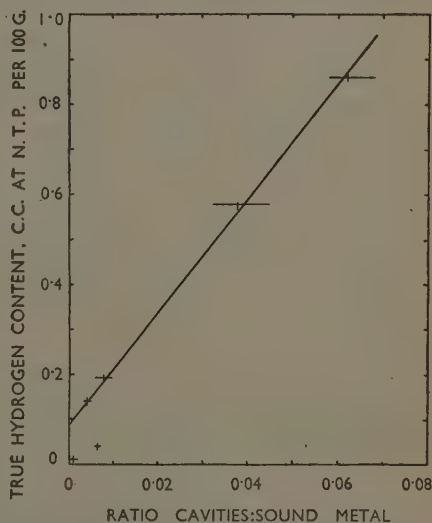


Fig. 1.—Relation between Cavity : Metal Ratio and True Hydrogen Content (horizontal line denotes range of experimental values).

have some hydrogen segregation) and has been neglected in drawing the calibration line; if, however, the best line had been drawn taking it into account, the effect on the estimation of hydrogen content in this range would not be very large. The intercept on the hydrogen-content axis cannot be given a definite interpretation in terms of solubility

of the gas in the metal, as not only are the conditions of solution ill-defined, but there are a number of disturbing factors (e.g. the absorption of hydrogen during the test from water held in the inevitable surface film) which may result in a parallel shift of the line from the theoretical position.

The largest standard deviation given in Table II (viz.: ± 0.0031 volume of cavities : volume of sound metal) represents a deviation of approximately ± 0.04 c.c. at N.T.P./100 g. in estimated gas content. The deviations of the single tests from the calibration line (Fig. 1) all fall within ± 0.10 c.c. at N.T.P./100 g., with the exception of material B, and for this the greatest error is 0.14 c.c. at N.T.P./100 g. In any case it is undesirable to place too much reliance on estimations at very low values of the voids produced, as here the possible occurrence of shrinkage porosity may introduce some scatter between different materials.

IV.—CONCLUSIONS.

A quantitative correlation has been found to exist between the voids formed in specimens of aluminium-7%-magnesium alloy sheet when immersed in molten potassium dichromate at 580° C. for 10 min., and the hydrogen content of the material determined by the vacuum-extraction method. This provides the means for a simple and rapid estimation of the hydrogen content of a wrought sample of this alloy to an accuracy, in the range investigated, of approximately ± 0.10 c.c. at N.T.P./100 g. The use of this method could probably be extended to other wrought aluminium alloys with comparatively wide freezing ranges.

The method is not likely, however, to prove appropriate for use with cast materials. The cast structure might not respond to the salt-bath treatment in the same way as a wrought one and pre-existent porosity might be of such a form that the escape of hydrogen from the thin specimen is permitted before or during the salt-bath treatment.

ACKNOWLEDGEMENTS.

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THE PHENOMENON OF ANISOTROPY IN 1187 ANNEALED POLYCRYSTALLINE METALS.*

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SYNOPSIS.

The conception of coefficients of partial uniform elongation e'_a and e'_b has been introduced, the value of which may be easily calculated from the data of elongation measurement on a fractured flat metal test-piece.

The relationship of these coefficients of partial uniform elongation :

$$K_a = \frac{e'_a}{e'_b}$$

is the coefficient of anisotropy for polycrystalline metals. It is a constant value for a given annealed metal, provided that the individual layers have undergone annealing before the same degree of cold working.

In drawn test bars, various layers of which have been submitted to different degrees of cold working, the coefficient K_a varies in a continuous manner from one layer to another.

Some annealed metals, such as mild steel, brass, and aluminium, after a previous cold working, show a distinct tendency towards anisotropy.

I.—INTRODUCTION.

ANISOTROPY of mechanical properties in annealed polycrystalline aggregates has been the subject of numerous investigations over a long period.

Thus, in 1929 von Göler and Sachs¹ called attention to the fact that annealed sheets of silver and brass show different mechanical properties in test specimens cut in different directions to the direction of rolling. Schmid and Wassermann² in 1931 observed a similar phenomenon in aluminium sheets.

The phenomenon of anisotropy of mechanical properties takes the most remarkable form in annealed copper sheets, as was shown in the joint work of Fahrenhorst, Matthes, and Schmid³ in 1932. J. Weerts⁴ also obtained similar results in 1933.

After these first exploratory papers a series of publications appeared which demonstrated that nearly all annealed metals which have undergone cold working, show anisotropy of mechanical properties, depending on the angle between the direction of rolling and the direction of the machined test specimen.

The present work deals with the investigation of a new form of

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mechanical anisotropy. In order to determine this anisotropy, it is not necessary to examine a series of test-pieces cut in different directions to that of cold working; the study of one test-piece alone is sufficient.

II.—THEORETICAL PRINCIPLES.

First, let us consider the phenomena that appear during the tensile testing of a flat test-piece made of a plastic metal. Such a test piece is made up of the gauge-length, denoted in Fig. 1 as l_{0M} , of the parallel section l_p , and of the ends.

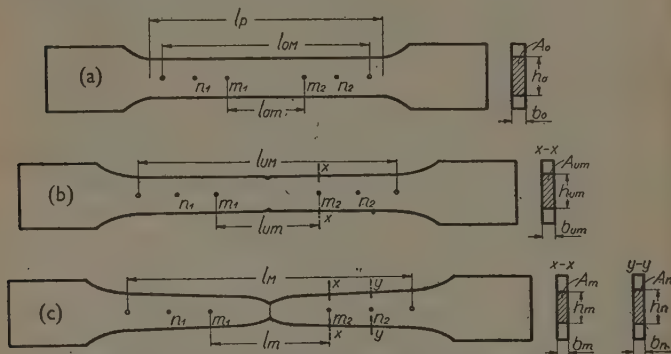


FIG. 1.—Illustrating the Three Stages of Deformation of a Test-Piece: (a) Initial state; (b) at the moment of reaching the limit of uniform elongation; (c) after fracture.

The various stages of the deformation of a test-piece are shown in Fig. 1. Fig. 1 (a) represents the test-piece in the initial state; Fig. 1 (b) corresponds to the moment when the test-piece has reached the limit of uniform elongation and the "waist" is being formed; finally, Fig. 1 (c) shows the test-piece after fracture.

Taking any points m_1 and m_2 on the test-piece symmetrically placed in relation to the centre of the test-piece, since A_0 is the cross-sectional area of the parallel section of a test-piece in the initial stage, and A_m the cross-sectional area of the test-piece after fracture in points m_1 and m_2 (Fig. 1), the coefficient of local elongation e'_m of the broken test-piece may be calculated from the formula :

$$e'_m = \frac{A_0}{A_m} - 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The coefficient e'_m for a given test-piece after fracture has a variable value depending on the position of the points m_1 and m_2 . This coeffi-

cient diminishes when these points are distant from the "waist" of the test-piece.

On a given broken test-piece a point can be found where the influence of the ends and the "waist" is equal, so that the cross-sectional area

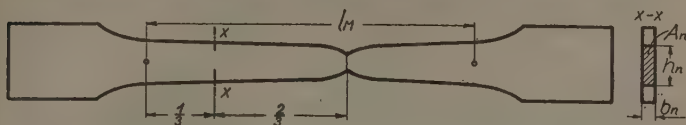


FIG. 2.—Position (X—X) of Measurement on Broken Test-Piece to Determine Coefficient of Anisotropy.

of the test-piece at that point A_n is equal to the cross-sectional area A_{um} . Such a position corresponds to the points n_1 and n_2 , for which the following equation proves true :

$$A_{n(c)} = A_{um(b)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The coefficient of local elongation for the points n_1 and n_2 is calculated from the formula :

$$e' = \frac{A_0}{A_n} - 1 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It has a constant value characteristic of the plastic properties of a given metal. The value e' is termed the coefficient of uniform elongation.

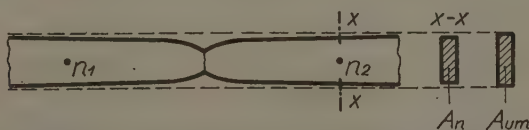


FIG. 3.—Position (X—X) of Measurement on Broken Test Strip to Determine Coefficient of Anisotropy, in Case where Ends of Strip are not Enlarged.

It follows that the points n_1 and n_2 may be approximately determined by the use of Fig. 2. The position (X—X) corresponds to the size of the cross-sectional area A_n , even when the test-piece breaks asymmetrically, on the condition, however, that the longer part of the broken test-piece is used for the calculations.

Let us now consider the tensile test of an ordinary strip in which three phases may also be discerned. The test strip after fracture will take the form shown in Fig. 3. The coefficient of uniform elongation would be calculated according to the formula :

$$e' = \frac{A_0}{A_{um}} - 1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

However, the size of the cross-sectional area at the end of uniform elongation A_{um} cannot be precisely determined. If instead of the value A_{um} in formula (4) the minor value A_n is substituted, then the correction $\Delta e'$ must be introduced to obtain the real value of the coefficient of uniform elongation e' . In such a case formula (4) will take the form:

$$e' = \frac{A_0}{A_n} - \Delta e' - 1 \quad . \quad . \quad . \quad . \quad (5)$$

Here, the area A_n should be measured at a point removed from the fracture, in order that the correction $\Delta e'$ may be as small as possible, as shown in Fig. 3.

The experiments of Krupkowski and Wantuchowski⁵ showed that the correction $\Delta e'$ may be calculated from the relationship:

$$\Delta e' = \frac{\frac{c}{1-c} - e'}{(Km + 1)^2} \quad . \quad . \quad . \quad . \quad (6)$$

where: e' is the uniform elongation;

c is the reduction in area at fracture;

K is a coefficient: $K = 0.5 + \frac{c}{1-c} - e'$;

m is the reduced length of a part of the test-piece,

where $m = \frac{l_{0M}}{d_{of}}$, d_{of} being the original diameter of the test-piece if its section is circular, and an equivalent quantity if otherwise. Therefore, for a flat test-piece $m = l_{0M} : 2 \sqrt{\frac{bh}{\pi}}$, b being the thickness and h the width of the test-piece.

In this way the coefficient of uniform elongation e' can be deduced on the basis of the tensile test of test-pieces with enlarged ends or of ordinary strips.

The problem of the so-called coefficients of partial uniform elongation must now be explained. To make clear this conception, let us examine the unit section of a strained test-piece of unit gauge-length corresponding to the points n_1 and n_2 in Fig. 1. Let us suppose that during deformation an inequality arises:

$$\frac{b_n}{b_0} < \frac{h_n}{h_0} \quad . \quad . \quad . \quad . \quad (7)$$

which shows that the metal during the tensile test contracted more towards direction b than towards direction h .

This deformation may be divided into two theoretical stages as shown in Fig. 4. In the first phase (a) \rightarrow (b) the deformation of the

metal takes place at the expense of the thinning of the test-piece towards b_n at a constant width h_0 ; in the second phase (b) \rightarrow (c), on the other hand, the thickness of the test-piece b_n will remain constant, and only its width will diminish.

According to the schematic diagram of deformation given in Fig. 4 the coefficients of partial uniform elongation e'_b and e'_h can be deter-

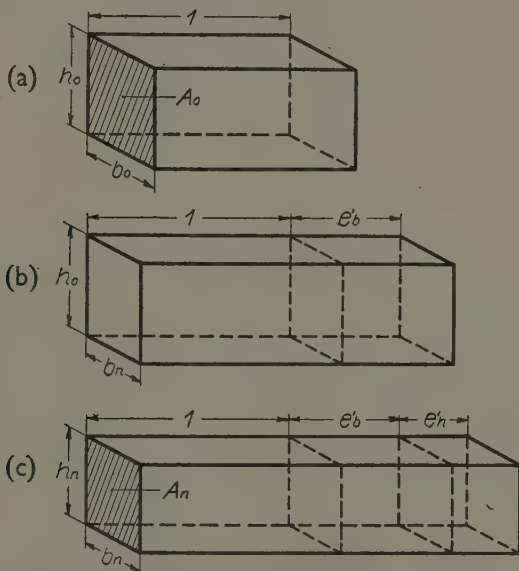


FIG. 4.—Schematic Representation of the Straining of a Unit Section of a Test-Piece until it Reaches the Limit of Uniform Elongation. e'_b and e'_h are coefficients of partial elongation.

mined. The value of the first coefficient depends on the reduction in thickness, and that of the second one on the reduction in width. These coefficients can be calculated from the relationship :

$$e'_b = 0.5 \left[\left(\frac{b_0}{b_n} \right)^2 - 1 \right] \quad . \quad . \quad . \quad . \quad (8)$$

$$e'_h = 0.5 \left[\left(\frac{h_0}{h_n} \right)^2 - 1 \right] \quad . \quad . \quad . \quad . \quad (9)$$

From equations (8) and (9) the sum of the partial elongations is found :

$$e'_b + e'_h = 0.5 \left(\frac{b_0}{b_n} - \frac{h_0}{h_n} \right)^2 + \frac{b_0 \cdot h_0}{b_n \cdot h_n} - 1 \quad . \quad . \quad (10)$$

The coefficient of total uniform elongation may be found from formula (3):

$$e' = \frac{b_0 h_0}{b_n h_n} - 1 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

By comparison of (10) and (11):

$$e'_b + e'_h = e' + 0.5 \left(\frac{b_0}{b_n} - \frac{h_0}{h_n} \right)^2 \quad . \quad . \quad . \quad (12)$$

The experimental data show that the value $0.5 \left(\frac{b_0}{b_n} - \frac{h_0}{h_n} \right)^2$ is so small that it can be practically considered as equal to zero, that is:

$$0.5 \left(\frac{b_0}{b_n} - \frac{h_0}{h_n} \right)^2 \approx 0 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Hence equation (12) takes the form:

$$e'_b + e'_h \approx e' \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which means that the sum of the coefficients of partial uniform elongations is equal to the coefficient of general uniform elongation.

In the case where the ends of a test-piece are enlarged, the coefficients e'_b and e'_h can be calculated from the measurement data in the position shown in Fig. 2. An ordinary strip, however, should be measured at points n_1 and n_2 (Fig. 3), and the initial distance between the points of measurements l_{on} should be at least equal to 6 equivalent diameters, i.e. $l_{on} \geq 6d_{of}$. Care must also be taken that the test strip is not too short, because then the grips of the machine would check its strain.

III.—ANISOTROPY OF ANNEALED METALS.

Tensile tests were carried out on flat test-pieces cut in the direction of rolling from sheets or rectangular bars of any annealed metal. It was observed that the specimens were reduced in thickness and in width in a different degree. This phenomenon is expressed by the inequality formula (7). Such behaviour in a metal can be explained by anisotropy. Therefore, a coefficient of anisotropy of metals K_a may be introduced. This coefficient is calculated from the formula:

$$K_a = \frac{e'_h}{e'_b} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Inequality $K_a \geq 1$ shows that the metal is anisotropic, and the degree of its anisotropy increases the more the value of the coefficient K_a differs from a value of 1. Only in a special case where $K_a = 1$ can a given metal be considered as isotropic.

1. Anisotropy in Bars of Annealed Metals.

To demonstrate the phenomenon of anisotropy test-pieces were cut from cold-worked and annealed rectangular bars according to the method shown in Fig. 5. Ten-fold test-pieces were used in these experiments, which means that the value of the reduced length calculated from the formula $m = l_{0M} : 2\sqrt{\frac{bh}{\pi}}$ was such that $m = 10$.

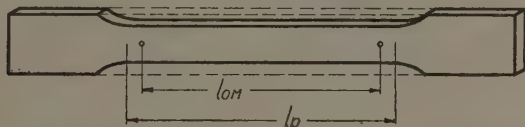


FIG. 5.—Method of Cutting Test-Pieces, 12×4 mm., from a Rectangular Bar, 20×4 mm.

Test-pieces thus obtained were annealed at suitable temperatures, and afterwards submitted to the tensile test. Measurements of the thickness and width of the test-pieces after fracture made possible the calculation of the coefficients of partial elongation according to formulæ (8) and (9), and then of the coefficients of anisotropy from equation (15).

Table I and Fig. 6 present the results obtained after fracture of an aluminium test-piece which had been annealed for 2 hr. at 500°C .

TABLE I.—Coefficients of Anisotropy of Flat Test-Piece of Aluminium Annealed for 2 hr. at 500°C .

Cross-section within the limits of the gauge-length 12×4 mm.

Point of Measurement Expressed in Terms of d_{of}	$2e'_h$	$2e'_b$	K_a
-0.5	14.68	39.40	0.373
0.0	21.84	41.96	0.520
0.625	22.23	41.96	0.530
1.250	22.22	41.96	0.530
1.875	22.87	42.80	0.534
2.500	22.87	43.71	0.523

From the course of the curve K_a it appears that the value of this coefficient over a large section of the gauge-length of the test-piece at distances removed from the fracture, is constant. Its average value is $K_a = 0.527$.

In a similar way experiments were carried out on other metals, using ten-fold test-pieces also prepared from bars of cross-section 20×4 mm. The results obtained are shown in Table II. From this

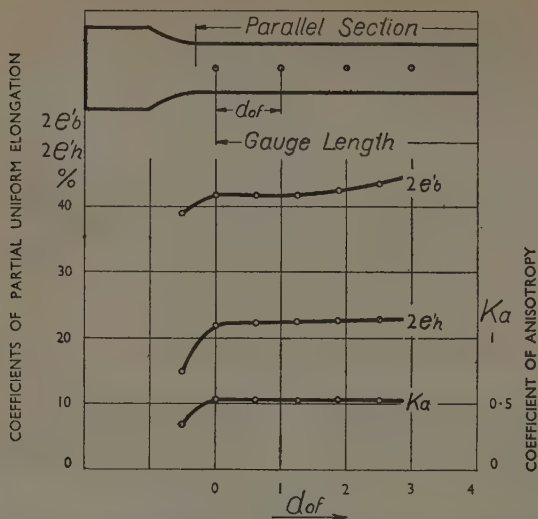


FIG. 6.—Coefficients of Anisotropy in an Annealed Aluminium Test-Piece, 12×4 mm., Cut from a Rectangular Bar, 20×4 mm. d_{of} is the equivalent diameter.

Table it will be seen that mild steel has the highest anisotropy, and copper the lowest.

TABLE II.—Coefficients of Anisotropy of Test-Pieces Cut from Rectangular Bars 20×4 mm.

Cross-section within the limits of the gauge-length 12×4 mm.; the relationship $h_0 : b_0 = 3$.

Metal	Temperature and Time of Annealing	Yield Point, kg./mm. ²	Ultimate Stress, kg./mm. ²	Coefficient of Anisotropy
Aluminium .	500° C.; 2 hr.	5.7	7.7	0.527
Copper .	500° C.; 2 hr.	6.3	21.8	0.875
Brass (70:30)	500° C.; 2 hr.	15.1	38.6	0.470
Mild steel .	700° C.; 2 hr.	20.6	33.6	0.349

2. Independence of Coefficient of Anisotropy of the Relationship between Width and Thickness of a Test-Piece.

The value of the coefficient of anisotropy is independent of the relationship $h_0 : b_0$ in a test-piece. It is a constant value, character-

istic for a given metal, provided that all the layers of the metal have undergone the same degree of cold working before annealing.

To prove this theory the following experiments were carried out. From a large sheet of mild steel, 4 mm. thick, test strips were cut in the direction of rolling. After annealing they were fractured. The relationship $h_0 : b_0$ in these bars was equal to 1 or 5. As will be seen from Table III the coefficient of anisotropy for all the test specimens is constant within the limits of experimental error.

TABLE III.—Coefficients of Anisotropy of Test Strips Cut from a Sheet of Mild Steel 4 mm. thick, Annealed for 2 hr. at 700° C.

Yield point 18.3 kg./mm.², ultimate stress 31.1 kg./mm.²

Number of Strip	1	2	3	4	5	6
$h_0 : b_0$	1	1	1	1	1	5
K_a	0.285	0.273	0.256	0.280	0.252	0.275

3. Dependence of Coefficient of Anisotropy on the Type of Deformation of the Various Layers.

It is interesting to examine in what degree the coefficient K_a will change when the various layers of the specimen have undergone different degrees of cold working before annealing. To solve this problem rectangular test specimens 20×4 mm. were used for the experiments. In such specimens the deformation of the various layers is different on account of the forces acting upon them during cold working, as illustrated in Fig. 7. In this Figure it is shown that the central portions of the bar deform differently from those near the edges.

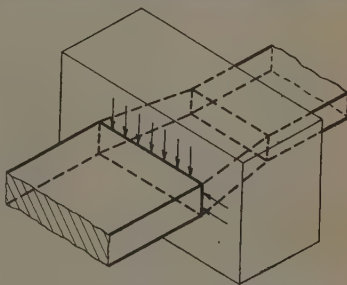


FIG. 7.—Illustrating the Forces Acting on a Rectangular Bar during Drawing.

Individual test strips from such bars were annealed, and after being fractured were measured. In this way the correct coefficient of anisotropy was calculated according to Fig. 4.

Tables IV, V, and VI, and Figs. 8, 9, and 10 present the experimental results. The metals tested, with the exception of copper, showed considerable anisotropy of the individual test-pieces. The curve of the coefficients of anisotropy in the test bars takes the form of a para-

bola, while the anisotropy of the test bar as a whole, denoted by the line AB , approaches the average value of the individual strips.

TABLE IV.—*Coefficients of Anisotropy of Copper Test Strips*
4 mm. thick, Annealed for 2 hr. at 500° C.

Number of Strip	1	2	3	4
$h_0 : b_0$	0.70	0.65	3.0	5.0
K_a	0.92	0.89	0.90	0.91

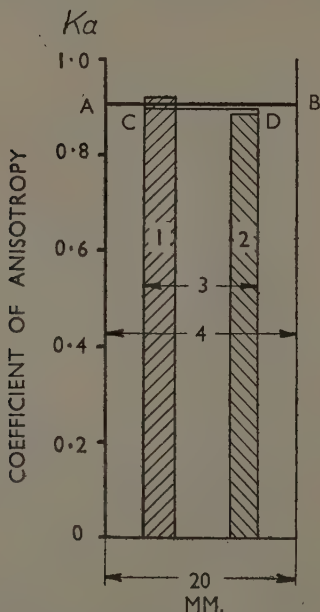


FIG. 8.—Results Obtained in Experiments on the Fracture of Test Strips of Annealed Copper.

Line AB marks the coefficient of anisotropy of the whole bar; the individual top lines refer to the anisotropy of its component strips.

4. *Anisotropy of Cylindrical Test-Pieces.*

The phenomenon of anisotropy takes place not only in rectangular flat test-pieces, but appears also in cylindrical ones. This is proved

TABLE V.—Coefficients of Anisotropy of Aluminium Test Strips
4 mm. thick, Annealed for 2 hr. at 500° C.

Number of Strip	1	2	3	4	5	6	7
$h_0 : b_0$	1	1	1	1	1	3.2	5
K_a	0.937	0.522	0.468	0.499	1.00	0.503	0.75

TABLE VI.—Coefficients of Anisotropy of 70 : 30 Brass Test Strips
4 mm. thick, Annealed for 2 hr. at 500° C.

Number of Strip	1	2	3	4	5
$h_0 : b_0$	0.98	0.97	0.62	1.03	5.0
K_a	0.850	0.407	0.373	0.935	0.760

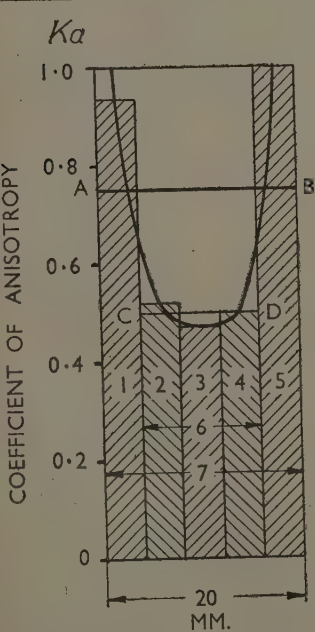


FIG. 9.—Results Obtained in Experiments on the Fracture of Test Strips of Annealed Aluminium.

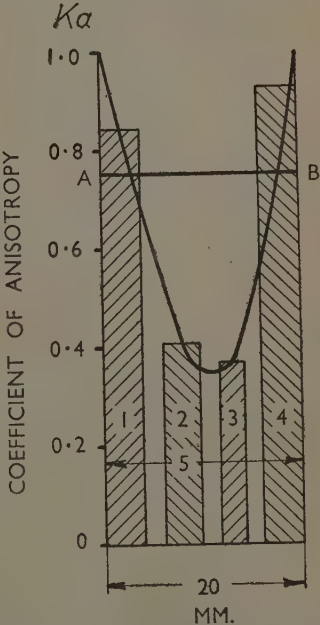


FIG. 10.—Results Obtained in Experiments on the Fracture of Test Strips of Annealed Brass.

Line AB marks the coefficient of anisotropy of the whole bar; the individual top lines refer to the anisotropy of its component strips.

by the following experiment. A cylindrical test-piece, 3.76 mm. in dia., was cut in the direction of rolling from an annealed steel sheet 4 mm. thick. After fracture it was found out that the cross-section of the test-piece changed from a circular to an elliptical one; here the ratio of the axis was equal to 1.77 in the "waist".

These experiments clearly indicate that the phenomenon of anisotropy appearing in annealed metals after cold working, is independent of the shape of the test-piece used.

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METALS IN CLOCK AND INSTRUMENT MANUFACTURE.* 1188

By R. E. TRICKER,† M.Sc., F.I.M., MEMBER.

SYNOPSIS.

The paper discusses the non-ferrous and ferrous metals generally used in the clock and instrument industry. The metals are dealt with in groups: turned parts, die-castings, pressed and blanked parts, spring materials, magnet alloys, and alloys with special applications.

Descriptions are given of leaded brasses and leaded steels which are suitable for Swiss-type automatic machines, particular emphasis being laid on tolerances, surfaces, and machinability. The three types of die-cast alloys principally employed—zinc-base, aluminium-base, and tin-base alloys—are illustrated by references to their uses.

Strip materials for blanking and pressing in leaded brass and steel are detailed with special regard to their freedom from stresses in such items as plates and wheels. In the spring section, mainspring materials—carbon and silico-manganese steel and the new Elgiloy—are discussed, giving analyses and methods of production. Alloys for hairspring manufacture are described and the reasons given for the choice of each alloy. Among the spring materials are grouped those for Bourdon tubes, diaphragms, capsules, and bellows, as these are all acting as spring materials stressed within their elastic limits.

Magnet alloys are dealt with briefly, as much information on this subject has been published elsewhere, but the great improvement in these alloys in the last few years is noted.

As an example of materials with special application, the magnetic compensating alloys of the Thermoperm and JAE type are quoted and their manner of application explained. Brief mention is also made of the use of sintered bronze bearings.

I.—INTRODUCTION.

THE clock and instrument industry has quite a long history, from the individually hand-built article to the mass-produced instrument of to-day. In the spring-wound clock and watch section practically the whole of the improvements have been in the metallurgy of the materials and in the automatic production machinery. As long ago as 1760 Harrison made a chronometer which only varied 5 sec. in two months on a voyage to Jamaica.

The introduction of the steam engine and the internal combustion engine gave rise to many demands for new instruments, followed later by the expansion of the electrical industry. The availability of A.C. with controlled periodicity produced a large demand for electric clocks. In common with many other processes, the mass production of instru-

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ments has only been rendered possible by the development of alloys suited to high-speed accurate machinery. This in turn has given an impetus to the machine tool maker to introduce faster machining rates, and so the cycle proceeds.

The clock and instrument industry now possesses many plants using moving-belt assembly methods producing thousands of completed units per day. To keep up the flow necessitates the unceasing supply of very accurately machined components in a wide variety of alloys and steels, and it is the aim of this paper to describe the metallurgical advances which have been made to meet this demand.

As so many varying metals must be included it is proposed to deal with them as far as possible in groups: turned parts, die-castings, pressed and blanked parts, spring materials, magnet alloys, and alloys with special application.

II.—TURNED COMPONENTS.

While many parts produced from rods are machined on the conventional automatic machines, such as Brown and Sharpe, B.S.A., Wickman, &c., a large proportion of small instrument work is carried out on special Swiss-type autos, including Bechler, Turnos, Peterman, Schaublein, and others. On these types the bar feed is through a canon bush necessitating very accurately dimensioned and good-surface bars. If the surface is at all scored or is roughly ground it will rapidly wear away the bushes and result in inaccurate dimensions on the finished parts. Further, if a bar is oval, an oval component will result. Therefore, the prime necessities for small bar work on Swiss-type autos are excellent finish and tolerances.

1. *Brass.*

Dealing first with brass, in order to obtain an accurate finish the leaded type is used, but it has been found necessary for small work to improve on the general British Standard Specification No. 249 as this is too wide as regards analysis, methods of manufacture, and size tolerances. To illustrate the difference, Table I gives a comparison between the two specifications.

It will be noticed that the copper range has been narrowed, as have the lead content and total impurities. Perhaps the greatest difference in the two specifications is in the close control of the tensile strength. The figures are higher, particularly for smaller rods, than the general run of B.S. 249 where only one minimum is given for all sizes. The higher figures are, of course, obtained by further cold work. Where it is necessary to rivet over the end of a component, a grade slightly higher in copper and lower in lead is used.

TABLE I.—*Brass Rod Materials.*

Specification	Analysis					
	Cu, %	Zn, %	Pb, %	Sn, %	Fe, %	Total Impurities, %
British Standard Specification No. 249	55-60	remainder	2-3.5	0.75 max.
No. 3 brass (S. Smith & Sons)	58-60	remainder	1.5-2.0	0.10 max.	0.10 max.	0.50 max.
794 (Imperial Chemical Industries Ltd., Metals Division)	60-63	remainder	2.0	0.75 max.
	Mechanical Properties					
	Size			Minimum Tensile Strength, tons/in. ²		
British Standard Specification No. 249	All sizes			25		
No. 3 brass (S. Smith & Sons)	Up to and including 2.50 mm.			38		
	2.50 to 5.0 mm.			36		
	5.0 to 10.0 mm.			34		
	Over 10 mm.			30		

2. Steels.

In a general survey of this nature, which endeavours to give an all-round view of clock and instrument metallurgy, it is obvious that ferrous and non-ferrous materials are inseparable, and that certain steels must be mentioned. The majority of pinions, spindles, many screws, arbors, &c., are turned, screwed, or gear-cut from steel rod on Swiss machines, and here again special steels have had to be worked out or adapted from existing specifications. For many parts sulphurized free-cutting mild steel is used. In order to produce a fine finish on small components the size and distribution of the sulphides are rather critical, and also it is desirable to keep the tensile strength in the region of 37-42 tons/in.² (170-200 D.P.N.).

This steel can be cyanide-cased to a depth of about 0.010 in. without detriment to the case, and is often used for bearing screws where a very hard surface is required. In inexpensive clocks and instruments, pinion teeth are usually run in the soft condition, but for higher-class movements hardened pinions are fitted. To improve the machinability of steels generally, lead is often added both to the sulphurized-type mild

steel and to the higher straight carbon steels up to 1% carbon. This addition cannot be detected under the microscope, and in the case of the higher-carbon steel has no adverse effects on the capacity to harden or on wear-resistance.

TABLE II.—*Carbon-Steel Rod Materials.*

Specification	Analysis					
	C, %	Si, %	Mn, %	P, %	S, %	Pb, %
Free-cutting (sulphur- containing)	0.15–0.20	0.30 max.	0.60–0.80	0.04 max.	0.20–0.25	...
Free-cutting (leaded)	0.12–0.15	0.20 max.	0.60–0.90	0.05 max.	0.20–0.25	0.15–0.25
No. 5*	0.40–0.45	0.30 max.	0.70–0.90	0.05 max.	0.20–0.30	...
No. 4L*	0.60–0.75	0.30 max.	0.70–0.80	0.05 max.	0.20–0.25	0.15–0.20
No. 3L*	0.60–0.75	0.30 max.	0.70–0.80	0.05 max.	0.20–0.25	0.15–0.20
No. 2L*	0.90–1.10	0.30 max.	0.40–0.80	0.05 max.	0.05 max.	0.15–0.20
No. 1L*	0.90–1.10	0.30 max.	0.40–0.80	0.05 max.	0.05 max.	0.15–0.20
	Mechanical Properties					
	Size			Tensile strength, tons/in. ²		
Free-cutting (sulphur- containing)	All sizes			37–42		
Free-cutting (leaded)	All sizes			37–42		
No. 5*	All sizes			50–60		
No. 4L*	All sizes			38–45		
No. 3L*	Up to and including 2.0 mm. Over 2.0 mm.			55–65 50–60		
No. 2L*	All sizes			42–46		
No. 1L*	Up to and including 2.0 mm. Over 2.0 mm.			60–65 50–60		

* S. Smith & Sons.

Table II shows the usual range of steels employed, and it will be observed that there are several types intermediate between the free-cutting mild and 1%-carbon. These are chosen according to the stresses involved and the hardness required. All contain either sulphur or lead.

It will be noticed that the analyses of Nos. 4L and 3L, and of Nos. 2L and 1L are similar. The difference lies in the amount of cold work applied to the rods. It is found that in very long spindles, for example, less distortion will take place using material with the lower initial tensile strength (i.e. Nos. 4L and 2L) than with the harder-drawn variety. There is a slight sacrifice, however, in machining speeds to give a good finish.

It is very important with parts which are to be hardened that there should be no decarburization on the surface of the rods, and a clause to this effect is included in most manufacturers' specifications. A close tolerance limit is also required on these rods. In many cases a \pm limit of 0.01 mm. or 0.0004 in., and in some rods \pm 0.005 mm. or 0.0002 in., is required. In general this can only be controlled commercially by grinding and reeling.

There are several types of pinion in common use to-day, namely, the leaf pinion, the lantern, and the die-cast lantern. Fig. 1 (Plate CXII) illustrates these varieties. The leaf type is cut on a special gear-cutting machine from turned auto blanks. The lantern type is a compound pinion using a high-carbon hardened steel wire threaded into a brass collar by special machines. The die-cast variety is assembled in the die and then pressure-cast with zinc alloy to form a complete unit.

III.—DIE-CASTINGS.

The materials most commonly used for die-castings are zinc-base, aluminium-base, and tin-base alloys. The usual composition limits are given in Table III.

1. Zinc-Base Alloys.

Great use is made of the saving in machining operations which can be effected by the introduction of zinc-base die-castings, both as case components and as internal supports for movements. Fig. 2 (Plate CXII) illustrates some of their various applications. The centre casting is the combined housing for a speedometer, oil-pressure gauge, and ammeter. The two top items are the cradle and end plate for a small motor. At the bottom left-hand corner is shown the internal cradle for a speedometer and at the bottom right-hand corner an oil pressure-gauge case and housing.

The main characteristics of the chosen alloy as adapted to instru-

TABLE III.—*Die-Casting Materials.*

Type	Analysis							
	Al, %	Cu, %	Mg, %	Fe, %	Pb, %	Cd, %	Sn, %	Zn, %
Zinc-base alloys (B.S. 1004A)	3.9– 4.3	0.03 max.	0.03– 0.06	0.075 max.	0.003 max.	0.003 max.	0.001 max.	remain- der
	Sn, %		Sb, %		Cu, %		Pb, %	
Tin-base alloys (a) (b)	75		20		5		0.35 max.	
	64–66		14–16		...		17–19	
	Si, %	Mn, %	Fe, %	Zn, %	Cu, %	Pb, %	Ti, %	Al, %
Aluminium-base alloys	10.0– 13.0	0.05 max.	0.60 max.	0.10 max.	0.10 max.	0.10 max.	0.20 max.	remain- der

ment work must be its ability for production to very accurate thin sections, its non-liability to corrosion, and its freedom from movement due to ageing. It has been found that the best all-round composition for work of this kind is the Mazak 3 or B.S.1004A type as detailed in Table III. With this alloy it is possible to work to a minimum wall thickness of 0.020 in., if required. Where used inside an instrument it is of paramount importance that no serious corrosion should take place, otherwise the rather bulky corrosion product would become detached and soon interfere with the sensitive mechanism. It is for this reason that the impurities must be very closely controlled, as it has been well established that it is the presence of very small quantities of tin, lead, and cadmium in conditions of normal humidity which leads to intercrystalline corrosion. For most applications a chromate treatment is given to the surface as an additional protection.

The last essential property is freedom from movement due to ageing after the instrument has been assembled. It does not need any explanation to appreciate that if the alloy expands or contracts it would interfere with the positions of sensitively set dimensions and so give rise to trouble. With an alloy such as that shown in Table III, there first occurs a shrinkage of the order of 0.00065 in./in. which is complete after 5 weeks' normal ageing, followed by an expansion of 0.00013 in./in. over about 3 years. It will be seen that the major movement is in the initial shrinkage.

For critical components it is usual to give an accelerated ageing of 3 hr. at 100° C. before final machining. After this it is found that the movement is negligible. The tensile strength of 16–18 tons/in.², with an

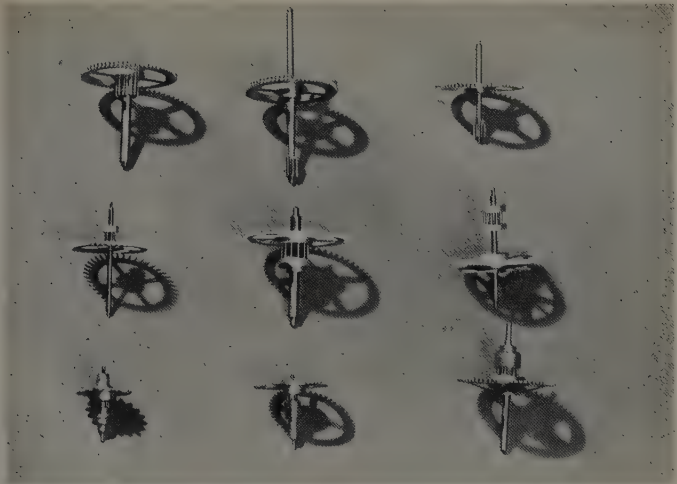


FIG. 1.—Types of Pinion and Wheel Assemblies. Top row : leaf pinions; middle row : lantern pinions; bottom row : die-cast lantern pinions. $\times \frac{1}{2}$.

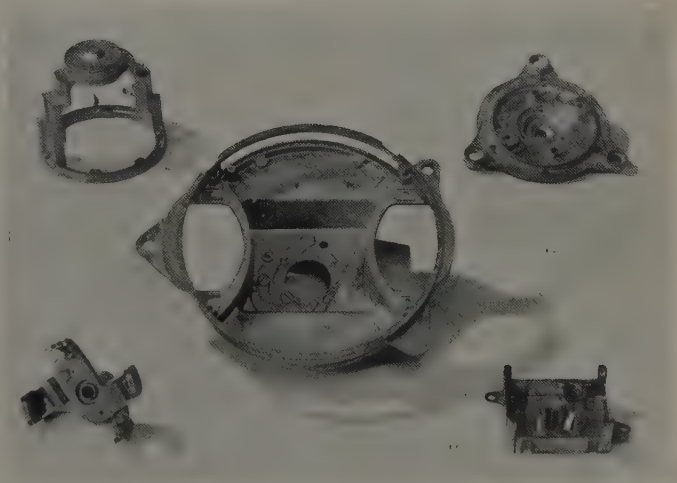


FIG. 2.—Typical Zinc-Base Die-Castings. $\times \frac{1}{4}$.

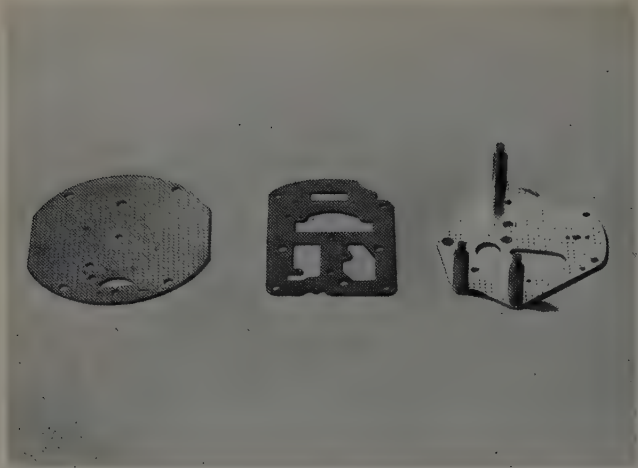


FIG. 3.—Types of Clock Plates Showing Amount Cut Away and Chequering. $\times \frac{1}{2}$.

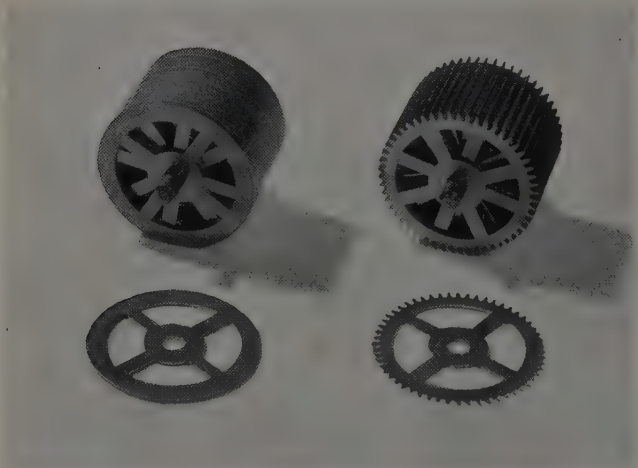


FIG. 4.—One Method of Producing Clock Wheels. Actual size.



FIG. 5.—One Method of Producing Bellows for Thermostatic Devices. $\times \frac{1}{4}$.

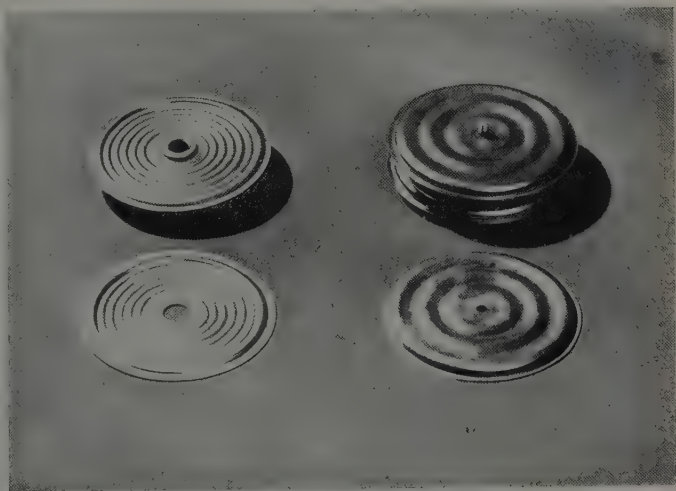


FIG. 6.—Typical Diaphragms and Capsules for Sensitive Pressure Measurements. $\times \frac{1}{2}$.

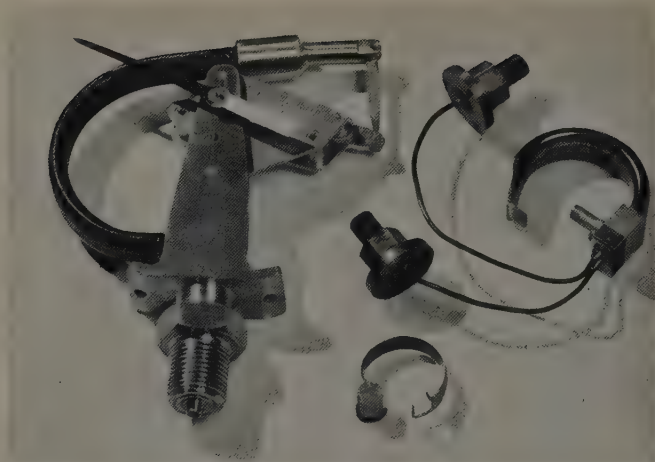


FIG. 7.—Bourdon Tubes : Steel (on left) ; Beryllium Copper (top right) ; Phosphor Bronze (bottom right). $\times \frac{1}{2}$.

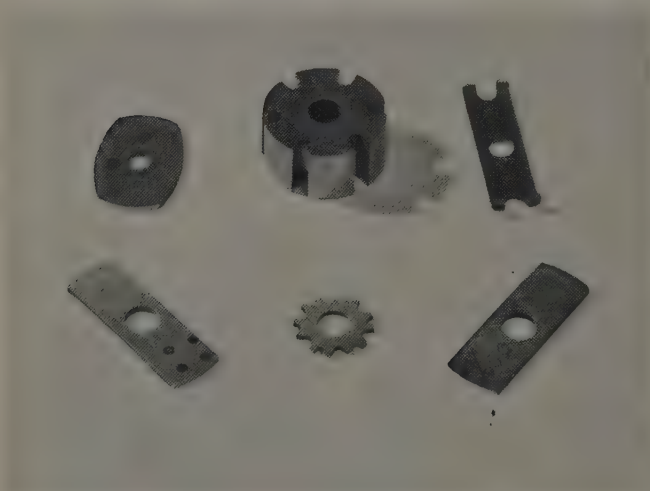


FIG. 8.—Instrument and Electric-Clock Magnets : Alnico (top centre) ; 15%-Cobalt Steel (left) ; 35%-Cobalt Steel (remainder). $\times \frac{2}{3}$.

impact value of 35–45 ft.lb. and a hardness of 60–70 D.P.N., are adequate mechanical properties for most constructional parts of instruments, but where used for wheels and moving barrels the properties are not so acceptable. Experiments have been made with both these items, without much advantage being shown, as compared with brass, owing (1) to the relative softness of the zinc-base alloy, and (2) to the rapid decrease of impact or shock properties as the temperatures are lowered to, say, -10°C .

2. Tin-Base Alloys.

The principal use of tin-base die-castings is for counters, such as are used on speedometers, and other integrating counter mechanisms. This alloy gives very sharp figures. On account of the high cost of tin, there is a tendency to change over to plastics of the polystyrene type.

The composition is now usually as shown in Table III; during the war more lead was added owing to the scarcity of tin.

3. Aluminium-Base Alloys.

These are used where advantage can be taken of their light weight, e.g. for cases of aircraft instruments. The 12%-silicon type is preferred for its ease of casting, but care must be taken when these alloys are to be anodized.

IV.—COMPONENTS BLANKED AND FORMED FROM STRIP.

1. Brass.

The most important parts produced by blanking are such items as plates and wheels, for which special brasses have been developed. The plates must perform two main functions, namely (1) to act as a support for the movement and to position each train of gears accurately in mesh; (2) to provide bearings for the spindles.

Plate strip must be dead flat and most important of all remain flat after stamping. Fig. 3 (Plate CXIII) shows how large an amount of material is removed from the inside of some plates, and unless the strip has been properly processed, remanent stresses will relieve themselves and buckle the plate slightly. This effect does not always take place immediately, and many clocks have been assembled and then after several days it has been found that the plates have warped. This results in the bearing holes canting over at an angle and binding up the gear train, in addition to altering end clearances. A bent plate can be corrected (although this entails an extra operation) by a method known as chequering. This is done by means of a press tool carrying a large number of small raised teeth and results in the effect illustrated in Fig. 3.

The pricking of numerous dents in the surface relieves the stresses and results in a plate which will stay flat. This operation is a palliative and should not be necessary, but some makers also employ it for decorative purposes.

It is essential that no burrs should be produced while stamping and piercing the holes, also that the small punches should withdraw easily. For this purpose lead is added to the brass and the strip cold rolled to a temper of 140–160 D.P.N. for plates and 160–190 D.P.N. for wheels.

As in many commercial clock movements the bearings of the pinions are merely holes in the plates, an α/β -brass mixture is preferred, the theory being that the harder β particle takes the load in an α matrix. Bearing these requirements in mind, the specification shown in Table IV has been found the most suitable.

TABLE IV.—*Plate and Wheel Brass.*

Use	Analysis				Hardness, D.P.N.	Tensile Strength, tons/in. ²	Elongation, % on 2 in. (0.25 in. wide test-piece)
	Cu, %	Pb, %	Total Impuri- ties, %	Zn, %			
For plates and large wheels	58–60	1.5–2.5	0.5 max.	remain- der	140–165	33–37	7–15% up to 3 mm. thick 7–20% from 3 mm. to 6 mm. thick
For wheels	58–60	1.5–2.5	0.5 max.	remain- der	160–190	37–40	3–9% for all thick- nesses

Fig. 4 (Plate CXIII) shows one method of producing clock wheels in large-scale production, using this brass. The teeth are hobbled in a stack of pressed blanks on a mandrel by a special automatic machine, and the mandrel is then removed. Some manufacturers blank wheels straight out complete with teeth, but in any case the qualities required of the brass are the same, i.e. no burrs must be formed.

Where a plate or other similar component has some portion with a slight bend in it, it is customary to use a leaded brass with higher copper and less lead to increase the percentage elongation a little.

Plates and wheels have been tried out in specially treated Duralumin and appear to be satisfactory. Brasses to the general lead-free specifications B.S. 265, 266, and 267 are used to a great extent for items such as bezels, slip-rings, cases, and similar parts which have to be formed or deep-drawn. As this is conventional practice no further reference need be made to these brasses.

2. Nickel Silver.

For escapement work small quantities of nickel silver are used. Although this does give some improvement in mechanical properties over the brasses, it is principally employed for the sake of appearance, as it obviates plating. Here again a special leaded type is used with about 2% lead and a nickel content of 12-15%.

3. Steel.

Quite a number of parts are blanked from steel strip. In the case of clock and watch hands, which have to be blued, it is found necessary in order to produce a good colour that the carbon shall be kept high. The practice, therefore, is to blank them either from a 0.9%-carbon strip or from mild steel and then to cyanide-case-harden them. This is followed in either case by hardening, polishing, and temper blueing.

This 0.9%-carbon steel strip is used in practically all small work, such as spring washers, friction discs, release springs, &c. Another application is for steel escape wheels which have to be hardened. The main requirements in this strip as supplied are perfect spheroidization of the carbides for ease in cutting and hardening, and a good surface. This steel will be mentioned again later in connection with mainspring materials.

It has been found necessary to call for rather different properties in the steel according to whether the components are to be blanked and formed, blanked only, or are to be gear-cut. The analysis is precisely the same, but the finishing technique employed by the suppliers has to be varied. These three types are illustrated in Table V.

TABLE V.—*High-Carbon Steel Strip for Blanking and Forming.*

Operation	Analysis					State of Material	Tensile Strength, tons/in. ²	Elongation, % on 2 in. (0.25 in. wide test-piece)	Hardness, D.P.N.
	C, %	Si, %	Mn, %	S, %	P, %				
Forming	0.9-1.10	0.30 max.	0.40-0.80	0.05 max.	0.05 max.	Fully annealed + 3-5% reduction by further cold rolling	180 max.
Blanking only	0.9-1.10	0.30 max.	0.40-0.80	0.05 max.	0.05 max.	180-220
Gear cutting	0.9-1.10	0.30 max.	0.40-0.80	0.05 max.	0.05 max.	...	48-60	5% max.	200-260

Many blanked and formed components are made from bright mild steel to one of the various temper specifications of the old B.S. 847 (1939)

which has recently been changed to B.S. 1449 (1948) and has a slightly different form. This type of work follows conventional lines, but as many such parts have to be plated, it is necessary to specify a good finish for the strip. Where a case is to be enamelled only, it is frequently pressed out from tinplate for additional corrosion-resistance.

Smaller quantities of aluminium strip are used for such items as pointers, where the weight of the moving part has to be considered.

V.—SPRING MATERIALS.

In this Section are grouped all the usual springs such as mainsprings and hairsprings, but it also includes the less obvious components, such as bellows, diaphragms, and Bourdon tubes. These parts are all acting as springs, the materials being stressed within their elastic range.

1. *Mainsprings.*

There are two main classes of mainspring materials in use to-day—the straight 1%-carbon steel and the silico-manganese steel.

The carbon steel is used mainly for the smaller table-type clocks and watches, while silico-manganese steel finds its principal application in the larger clocks and chime movements. The larger clocks use spring thicknesses of up to, say, 0.022 in., and it has been found that silico-manganese steel is less sensitive to slight deviation in heat-treatment in such thick sections and does not suffer the same proportion of breakages when wound round a small arbor. Before the 1939–45 war this country had to rely to a large extent on imported Swedish spring steel strip, but recently great strides have been made towards satisfying our own needs. There is now a very modern English plant producing most of this country's mainsprings and toy springs. In the majority of cases the hardened and tempered strip is supplied in large coils to the instrument and clock manufacturers, who make up their own springs. It is most important that the correct physical properties are maintained, and the tests applied usually include micro, tensile, D.P.N. hardness, and a 180° bend test round a specified diameter, according to the thickness of the strip. Watch springs are at present practically all made from 1.0–1.2% carbon steel, but a patent has recently been taken out in the U.S.A. by the Elgin Watch Co. for a material called “Elgiloy”. This is not really a steel; it has a nominal analysis as shown in Table VI, but this can be varied. It reacts as a precipitation-hardening alloy in the same way that beryllium copper can be hardened after only a final low-temperature treatment.

The conventional carbon steel spring strip is either oil- or air-hardened

TABLE VI.—*Mainspring Materials.*

	Analysis								Hardness, D.P.N.	Uses
	C, %		Si, %	Mn, %	S, %	P, %				
Carbon steel	0.95-1.05		0.3 max.	0.4 max.	0.025 max.	0.025 max.		540-700 (according to section)	For all ranges of clock and watch springs	
Silico-manganese steel	0.55-0.65		1.80-2.20	0.70-1.00	0.035 max.	0.035 max.		540-620 (according to section)	Mainly used for larger clock springs	
	Co, %	Cr, %	Ni, %	Fe, %	Mo, %	Mn, %	C, %			Be, %
Elgiloy	40	20	15.5	15	7	2	0.15	0.03	640-700 (small sections)	For watch and special small springs only

from about 780°–800° C. and then tempered back in the neighbourhood of 260°–320° C., according to the desired properties and thickness of the strip. With Elgiloy the billets are hot rolled to about 0.050–0.060 in. and then solution-treated at about 1100°–1200° C. In this condition the alloy can be cold rolled to the thickness of watch springs, say, 0.004–0.006 in., without intermediate anneals. The final properties are brought out by a precipitation-hardening treatment of about 5 hr. at 480° C. It is claimed that the alloy is non-magnetic and immune from corrosion. Typical analyses and hardness figures for all these materials are shown in Table VI.

2. Hairsprings.

Hairsprings are an extremely important part of very many clocks and instruments. As several different materials are used for hairsprings according to the function they have to perform, their various uses will first be outlined and each dealt with individually later.

The commonest spring in use to-day is made from phosphor bronze, usually containing 7–8% tin. This can be easily cold worked to give quite considerable tensile strength in the small size of wire used, and if care is taken with the setting temperature a reasonably elastic spring can be consistently produced. Such springs have to a large extent superseded the steel hairspring, which suffers from corrosion trouble both in storage and use. They are generally employed in cheap alarm clocks, where temperature compensation is not a great advantage, owing to the fact that there are greater errors in the components and assembly which

prevent such clocks from being regulated to seconds per day. Another large use for phosphor bronze is in "zero-izing" springs where the pointer of an instrument has to work against its torque and be returned to zero when the stress is removed. Such an application is very well illustrated in the magnetic speedometer fitted to the majority of cars.

With fine watch movements and good-class clocks the balance must be compensated for temperature differences to allow the mechanism to keep time. In the past this was accomplished by a split balance using a bi-metal rim with a steel hairspring, but this is very costly to make and, apart from chronometers and certain very high-class watches, it is now customary to use a solid brass or nickel-silver balance wheel and to compensate its expansion with the hairspring. Such a hairspring must be made from a substance having a practically nil or slightly positive thermo-elastic coefficient, and these materials have been developed from the original Invar to the Elvinar type common to-day. There are several variations of this alloy, but they all function in the same way. Another by no means unimportant advantage is that it is not so susceptible to magnetism as steel.

When an instrument hairspring has to carry an electric current phosphor bronze suffers from the disadvantage of having only 10-20% of the conductivity of copper, so a cadmium-copper alloy is often used for delicate applications such as galvanometers, milliammeters, &c. This will give a conductivity of 80-90%, but the springs need very careful handling as they are rather soft. Where a spring is to be highly stressed and take large deflections it is usual to employ beryllium copper. This material can be hardened up to approximately 350-400 D.P.N., gives a robust spring, and does not suffer much from drift. This latter quality is very important, particularly with aircraft instruments such as high speed revolution counters, where the total permissible error may be only 0.5%. The alloy is also, of course, resistant to corrosion.

Before proceeding to the chemical and physical characteristics of the alloys used, the method of producing hairsprings may be outlined. The wire is obtained from the manufacturers to a specified controlled analysis and in the soft condition, i.e. it has been close- or strand-annealed to remove the effects of cold work. The size is calculated according to the amount of cold work which the hairspring manufacturer intends subsequently to apply to the wire. After the wire has been accepted it is drawn down with a carefully controlled draft through diamond dies to final size, cleaned, and rolled through highly finished rolls to a ribbon. This flattening should preferably be accomplished in one pass and gives a ribbon with a width : thickness ratio of, say, 8 : 1.

When it is realized that the torque of a hairspring varies as the cube of the thickness it will be appreciated that the accuracy of the ribbon must be of a high order, and it is commonly measured in production to 1/1000 of a millimetre, or 0.00004 in. The springy ribbon is cut to length as it leaves the rolls and is wound into a "box" (open on one side) for setting to a spiral. The number of pieces in a box determines the pitch of the spring, and it is necessary so to set the ribbon that it retains this form. This is accomplished by heating the box, either on a hot plate or in a small furnace with gas protection to avoid staining, for a sufficient time to remove the coiling stresses. The temperature and time vary, of course, with the alloy, but with the exception of precipitation alloys of the beryllium-copper type the time is of the order of a few minutes.

When cold, springs will fall from the box or can be separated quite easily by shaking gently in a small bottle. The springs are then mounted on collets or centre-pieces so that they can be attached to their spindles.

TABLE VII.—*Hairspring Materials.*

	Approximate Analysis	Young's Modulus, E , lb./in. ² $\times 10^6$	Electrical Conductivity of Copper, %	Uses
Phosphor bronze	Sn 7, P 0.25%, remainder Cu	16	16	General use for clocks and return springs
Beryllium copper	Be 1.9-2.1, Co 0.3%, remainder Cu	18	25-30	Used for highly stressed springs
Cadmium copper	Cd 1.0%, remainder Cu	18	85-90	Used where high conductivity is essential
Elinvar	Ni 35, Cr 8, O 0.06%, Mo, Si, &c., remainder Fe	23	...	Used for temperature compensation, as in watches
Metelinvar	Ni 40, Cr 6, W 3, Mn 2, Mo 1.5, O 0.60%, remainder Fe	24	...	Used for temperature compensation, as in watches
Nivarox	Ni 35, Cr 8, Ti 1.0, Be 0.8, O 0.06%, remainder Fe	25	...	Used for temperature compensation, as in watches
Steel	O 0.90-1.10%	28	...	Used in a few clocks; also watches with bi-metallic balance

The analyses and physical properties of the common hairspring alloys are shown in Table VII. The formula for calculation of the torque is:

$$T = \frac{E b D t^3}{12 L}$$

where :

T = torque in dynes-cm.²

E = Young's modulus in dynes/cm.²

b = width of strip in cm.

t = thickness of strip in cm.

L = length of strip in cm.

D = full-scale deflection in radians.

It will be noticed that Young's modulus E enters into the calculation and, contrary to some statements, it is definitely found that this varies according to the degree of cold working of the strip. Any initial calculation for a hairspring can, therefore, only be approximate and exact dimensions are obtained by trial springs.

For temperature-compensation alloys a Coulomb's pendulum is used to show the variation of the elastic modulus with temperature. Each batch of material is usually checked. The final checks are taken with a standard watch under controlled heat conditions.

The following Sections deal with spring components of a different nature, i.e. bellows, diaphragms, and capsules, which are produced from strip.

3. *Bellows.*

Bellows are principally used in expansion devices such as car thermostats, and as they are severely worked during their manufacture are commonly made from 80 : 20 brass or Tombac.

Fig. 5 (Plate CXIV) shows the sequence of operations followed by one manufacturer in forming the complete bellows. The starting point is a plain disc which is deep-drawn in stages with appropriate anneals until one arrives at the final thin-walled tube. This is then spun up with a spinning tool into a series of convolutions giving the correct collapsed length of the bellows. This process very slightly thins the wall at the extreme edge and so tends to produce a very flexible unit. There are other ways of making these bellows, namely the hydraulic method where the tube is collapsed by internally applied hydraulic pressure, also a method of stamping out slightly formed blanks, turning the edges over, and soldering. Such a bellows is shown at the front left-hand side of Fig. 5. If this latter method is used 70 : 30 brass is often specified, but other metals can be used.

4. *Diaphragms and Capsules.*

Capsules are in effect a single-unit bellows, as shown in Fig. 6 (Plate CXIV). They are used in altimeters and air-speed indicators, and must be rendered very sensitive in order to respond to small differences in height

by the change in barometric pressure, or pressure from the Pitot tube in the case of the speed indicator. Obviously, the thinner they can be made, consistent with strength, the more sensitive they will be, and the materials usually employed are phosphor bronze and beryllium copper. Important points to be taken into account are freedom from drift, i.e. failure to return to the zero position after stressing, and from hysteresis which shows itself by producing different readings in ascending the pressure scale to those given on descending.

A typical material is standard beryllium-copper strip about 0.005–0.007 in. thick, containing 1.9–2.1% beryllium with up to 0.3% cobalt for grain refinement. Round corrugated blanks are stamped from the solution-treated strip. The corrugations are added to give strength and the correct characteristics to the capsule. These blanks are then heat-treated to produce precipitation-hardening to the degree required, which may not necessarily be the maximum obtainable. The edges of the blanks are next soldered up by various methods dependent upon the applications intended, but for some instruments brazing is adopted. It should be possible to use induction heating for this purpose.

5. Bourdon Tubes.

An example of a tube acting as a spring is the Bourdon tube as used in pressure gauges. Phosphor bronze can be employed up to pressures of 1000 lb/in.², after which it is usual to change over to beryllium copper and steel. A Bourdon-tube section, as shown in Fig. 7 (Plate CXV), is oval with a wall thickness varying between 0.005 and 0.040 in., according to the pressures involved. When phosphor bronze is used the tube is preferably of a hardness between 140 and 160 D.P.N., while beryllium copper is supplied in the solution-treated condition. The first step is to cut to length and bend. A jig has been made which will bend these tubes without filling if the production is large; the alternative method is to fill with either common table salt or Cerrobend. These latter fillers are subsequently boiled out and the tube thoroughly cleaned and dried.

Low-pressure Bourdon tubes in phosphor bronze are usually given a stress relief of 280° C. for 1 hr. to eliminate subsequent drift. The end-pieces are then soldered into the phosphor-bronze tube, making sure of removing all flux.

It will be noticed how the accent on drift keeps recurring and how important it is that many of the materials for clock and instrument manufacture should be as stress-free as possible. The point has been mentioned in connection with plates, capsules, Bourdon tubes, and hairsprings.

With Bourdon tubes made in beryllium copper a slightly different

technique is used. After bending in the solution-treated condition, the end-pieces are silver-soldered in for strength and then the whole assembly is given the precipitation-hardening treatment. As the temperature employed is well below the melting point of the silver solder this treatment gives a very stable tube.

Steel tubes for higher pressures are usually made from a chrome-molybdenum steel containing about 0.35–0.45% carbon, 1% chromium, and 0.25–0.40% molybdenum. The tubes are formed in the soft condition after which they are hardened at 900° C. and tempered at about 400° C. After sand-blasting they are given a stress relief to prevent zero shift. The ends are screwed into their end blocks with molten solder to ensure a pressure-tight joint. Owing to the difference in modulus of elasticity between phosphor bronze and steel, a greater deflection can be accommodated with the former without increasing the gearing ratio.

6. Wire.

Before leaving spring materials an interesting application may be mentioned of wire in flexion. This is the driving flex, which is a very important part of some instrument work, notably speedometers, and is made by taking a central wire and wrapping round it several layers—three, four, or up to seven—according to the strength required. Each layer is laid at a different angle to the one beneath it and is wound four or five wires at a time. Thus a flex is usually known as “four start 3½ mm.”, for example.

The material for the wires is usually a patented 0.40–0.50% carbon steel giving a tensile strength of 95–120 tons/in.²

VI.—MAGNET ALLOYS.

Small magnets are used in many instruments, such as the magnetic speedometers fitted to most cars and, of course, synchronous electric-clock movements. The range is illustrated in Fig. 8 (Plate CXV).

Most of them are produced as hot stampings from strip, but special types are produced by powder metallurgy and from such alloys as Alni, Alnico, and finally Alcomax. As this subject has been fully covered by publications of the Permanent Magnet Association it is not proposed to elaborate it here.

Although it is the aim of the instrument manufacturer to make his products as light as possible, he does not always choose, say, Alcomax or Alnico automatically. Economics enter very largely into his choice, and also the ease with which the magnet can be produced. For instance, the problems arise of holes and of machining. Tungsten and chrome

magnets can easily be machined, but the difficulty becomes greater with the cobalt steels. The 3, 6, 9, and 15%-cobalt magnets can be machined, but it is increasingly difficult with the 35%-cobalt alloy. Alni and Alnico can only be produced as castings or by powder metallurgy, and holes are cast in. Any cleaning up must be done by grinding. The Alcomax alloys are also being used for special applications.

VII.—SPECIAL ALLOYS.

1. *Magnetic Compensation Material.*

Under this heading it is proposed to deal briefly with one or two alloys which have special applications. The first is a nickel-iron alloy usually known as Thermoperm with an analysis controlled to rather fine limits. It is used to secure compensation in a magnetic-type speedometer or tachometer, where the "drag cup", as it is called, is usually made of pure aluminium. The resistance of aluminium varies approximately $0.36\%/^{\circ}\text{C.}$, so that an error would be introduced into the instrument on either side of its calibration temperature. Compensation is obtained by arranging that the lines of force of the magnet shall be increased or decreased by a shunt across the poles. When the temperature rises the conductivity capacity of the shunt decreases and more lines of force are diverted to the magnet. With a fall in temperature the reverse occurs. The material employed then should show as nearly as possible a straight-line relationship between temperature and magnetic permeability; this, of course, becomes nil at the Curie point—another feature of this alloy which must be controlled. The composition is given in Table VIII.

TABLE VIII.—*Magnetic Compensating Alloys.*

	Analysis				
	Ni, %	Mn, %	Si, %	C, %	Fe, %
Thermoperm (nickel-iron alloy)	29.5 ± 0.3	0.55 ± 0.15	0.3 max.	0.15	remainder
	Ni, %	Cu, %			
JAE metal (nickel-copper alloy)	70	30			

The alloy is used in the form of pieces blanked from strip. Melts have to be made up to very close limits and their magnetic properties measured. This is such a sensitive business that only approximately

50% of the melts are usable. Another alloy for the same purpose is known as JAE metal, and has a composition approximately nickel 70, copper 30%. It has not such an intensive effect, and is limited to a much smaller range of temperature. Alternatively, it is possible to use an aluminium-manganese alloy giving a very low temperature/resistivity coefficient to correct the drag cup instead of having to shunt the magnet. Where it is possible to use a heavier drag cup a copper-nickel-manganese alloy of 94 : 4 : 2 composition is also available. This has a very low temperature coefficient of electrical resistance, but, of course, is handicapped for use in a very light, sensitive moving component by having a much higher density than the aluminium-manganese alloy.

2. Sintered Bronze Bearings.

In most clock and instrument movements it is difficult to re-oil the fast-moving side of the train, and normally the initial oiling of the bearings should last for a very long period, often years. A great deal of research has been carried out on oils which will not creep, gum-up, or freeze. This is rather outside the scope of the present paper, but mention may be made of the sintered bronze bearing. This type of alloy provides a constant reservoir of fresh oil and is used particularly in electric clocks and small motors where a very long bearing area has to be kept adequately lubricated. The normal oil content of sintered bronze bearings is 30 vol.-%, but they can be obtained to give 50 vol.-%.

These small bearings are made by powder metallurgy, with an analysis of approximately 10% tin with a small addition of graphite. It is usual for the instrument manufacturer to impregnate them with oil before assembly.

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THE NEW FACTORY OF THE SOCIÉTÉ CENTRALE DES ALLIAGES LÉGERS AT ISSOIRE (PUY-DE-DÔME) FOR THE WORKING OF LIGHT ALLOYS.*

By JEAN MATTER,† MEMBER, and MARCEL LAMOURDEDIEU.‡

SYNOPSIS.

About 1938, French light-alloy manufacturers began to study the desirability of setting up a large works for the rolling of bodywork sheet. The outbreak of war made the need more acute, and it was decided to erect a plant at Issoire. After the defeat of France in 1940 the equipment was set up in the United States, but the Issoire works was nevertheless constructed during the Occupation and after the war and has now been completed. The buildings and the plant which they contain are fully described.

I.—HISTORICAL INTRODUCTION.

IN 1938 the Société du Duralumin carried out, in conjunction with the Citroen Company, some investigations into the use of light alloys in motor-car construction. In view of the promising nature of some of these results, Citroen went some way towards developing a mass-produced small car, but a study of manufacturing requirements showed that, if this type of car met with any great success, the light-alloy producers would find themselves unable to supply the necessary quantities of sheet in the requisite quality. Citroen thereupon postponed the adoption of these car types. Obviously a car manufacturer could not be expected to cater for a particular design of car two years in advance of the installation by the fabricators of plant to provide the materials necessary for the production schedules; and it was apparent that the difficulty encountered in the case of Citroen was likely to arise in the case of any large user of sheet, automobile or otherwise. The Société du Duralumin therefore decided to tackle the problem of increasing its sheet output capacity.

The Société du Duralumin had kept in touch with the American Rolling Mill Company's research on the rolling of thin sheet, and was acquainted with the new plant installed in the United States for the continuous rolling of strip in the tin-plate industry and also for the

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production of bodywork sheet. A succession of visits by engineers to the U.S.A. in 1938 and 1939 led, firstly, to the placing of an order in July 1938 with the United Engineering and Foundry Co. (U.S.)—Chavanne Delattre (France) group for a four-high cold mill with rolls 1500 mm. in width, as the first unit of the proposed extensions; and, secondly, to plans for modernizing the Faremoutiers plant, consisting of one reversing mill and two continuous mill trains. These plans had been worked out by July 1939.

After the war broke out in September 1939, the French Government quickly recognized that the domestic capacity for Duralumin output was quite inadequate to meet national requirements for aircraft and armaments, and called upon the producers of light alloys to double their capacity. The producers decided that the most rapid and effective method would be to undertake the erection of new plant capable in itself of providing the desired increase in output. On 11 November 1939, a contract was signed placing the Société Centrale des Alliages Légers (S.C.A.L.) and their Issoire works in a position relative to the State similar to that which was later adopted in the United States, namely the State paid for everything, owned everything, and entrusted the management and operation of the plant to a competent industrial concern, with no gain other than the prospective opportunity of taking over the plant at an advantageous price after the war was over. The site of the Issoire works was chosen because of its remoteness from national frontiers and also because of the vicinity of the French grid.

On 12 November 1939 the Société Centrale des Alliages Légers (S.C.A.L.), a subsidiary of the re-rolling group, on the basis of plans prepared some months previously, placed an order in the United States for the plant and equipment necessary for the projected works. This comprised: for sheet, a hot reversing mill, one continuous three-stand strip mill, and two single-stand sheet mills; and for rolled sections one five-stand 600 mm. mill train; with all the accessory electrical gear. Two rod-mill trains (450 and 350 mm., respectively) were ordered in Belgium, and only an order for a blooming mill was placed in France. It was the policy of the Ministère de l'Armement to place orders for plant in the United States so that French industry would be left free to handle all the detailed orders for the armament factories.

In June 1940 the Armistice abruptly cut France off from the outside world. A four-high sheet mill, the first to arrive in France, was sent back to Halifax, while the remainder of the plant ordered was left in store at the New York docks. This plant, since it formed part

of a French Government order, was passed on by French orders to Great Britain and that country re-sold it in the United States to the Reynolds concern (who erected it as it stood at Lister Hill), since it was not considered useful to ship the plant to Britain. The plant was actually utilized as a pilot plant serving various American and British works.

S.C.A.L. was then in the position of having factory buildings three-quarters completed with nothing, or next to nothing, in the way of plant to put in them. The plans, however, were retained. The *Ministre de la Production Industrielle* agreed without delay to adhere to the original schedules modified only in some particulars. The production of rod, primarily an essential for fuse components, was cut out of the programme, as was also the section rolling mill for aircraft struts. The rolling mill for sheet and strip and the blooming department were kept; moreover, an extrusion press ordered by the *Ministère de l'Air* in 1939 from the Loewy Engineering Co. was added. Difficulties were, of course, encountered, but a solution was found for all of them.

The design of the sheet mills was left to S.C.A.L. Delattre et Frouard entered into an agreement with United Engineering to build the plant on the basis of these plans since, the distribution of steel being under German control, it was expedient that S.C.A.L.'s name should not appear except in the quarterly balance sheets. Neither mechanical nor electrical equipment was allowed to appear in the official records, and as a precautionary measure not even those electric motors for which complete components existed were assembled. As regards the Loewy press mentioned above, the cylinder sent to France in 1940 passed port after port until it ended up in Casablanca, where it was finally unloaded and remained until 1945. The remainder of the press was built bit by bit in Belgium and in France. The adaptation of the blooming mill from steel to light alloys was carried further since there was plenty of time to work on it.

The actual financial set-up was changed, S.C.A.L. having increased its capital and received loans from the French *Crédit National* in order to meet the outlay. The schemes worked smoothly; in point of fact the Occupation Authorities never interfered with the Issoire works or with the production of plant components in different French works. At the suggestion of the responsible French authorities the schemes were even carried so far as to risk buying, on the basis of ante-dated contracts, a Government-owned building which the Germans had requisitioned at Nantes (in the Occupation Zone), subsequently removing it and re-erecting it at Issoire (Unoccupied Zone). It will be

obvious, however, that the rate of erection of the plant was not very speedy, partly on account of the lack of permits for materials and partly because of the absence of any priorities.

At the time of the Liberation the position was as follows. The buildings for housing the sheet mill, the extrusion press, the blooming mill, and the first stage of the casting shop were completed. As regards plant, the adaptation of the blooming mill was well advanced, the extrusion press was two-thirds built, and two sheet mills out of six were in course of construction, without the Germans being any the wiser. By arrangement with the responsible authorities an order was placed in the United States for the four sheet mills which had not been commenced, and for certain plant for finishing operations such as shears, trimmers, and certain furnaces, the rest of the electrical gear and the remainder of the mechanical equipment being ordered in France. It was still a slow business owing to shortage of cement, iron and steel, and non-ferrous metals. At the present time, however, all the main plant has been delivered and the greater part erected and progressively started up. It may be of interest to mention one last mishap which occurred, when the Liberty ship "Ocean Liberty", carrying some of the plant ordered from the U.S., blew up in Brest roads in 1947 and had its cargo thrown by the blast all over the town. All this plant, of course, had to be replaced.

II.—GENERAL DESCRIPTION.

As indicated in the Historical Section the works, according to the plans of November 1939, were intended to cater for the production of:

- (1) Sheet and strip.
- (2) Extruded rod and sections.
- (3) Rolled rod and sections.

The respective procedures for these products were as follows:

1. *Sheet and Strip.*

(a) Melting alloys; (b) casting rolling slabs (rectangular); (c) scalping; (d) preheating slabs; (e) initial hot rolling; (f) intermediate annealing, if required; (g) second hot rolling; (h) annealing of hot-rolled strip; (i) cold rolling; (j) quenching or annealing; (k) levelling, shearing; (l) inspection, packing, and despatch.

2. *Extruded Rod and Sections.*

(a) Melting alloys; (b) casting round billets; (c) scalping; (d) preheating billets; (e) extrusion; (f) quenching or annealing; (g) shearing to length, trimming, &c.; (h) inspection, packing, and despatch.

3. *Rolled Rod and Sections.*

(a) Melting alloys; (b) casting square-section billets; (c) scalping; (d) preheating; (e) initial hot rolling in the blooming mill; (f) shearing to length and scalping; (g) preheating; (h) rolling rod and sections; (i) sawing-off, and quenching, or annealing; (j) trimming, cutting to length; (k) inspection, packing, and despatch.

In line with A.R.P. considerations ruling at the time, the various buildings were dispersed as far as possible over the 80-hectare site, while at the same time the internal arrangements were planned so as to provide for the minimum handling of scrap, such as swarf and chips, between buildings and for grouping plant in each building to reduce handling where a rapid sequence of operations was involved.

The net outcome was the erection of three main buildings :

(1) *The Foundry*, in which the melting of the various alloys and the casting of the different types of ingot used throughout the works is undertaken. To the foundry proper is attached the shop where the ingots are sawn and scalped. The blooming mill for the hot roughing of the rod stock is also adjacent to the foundry.

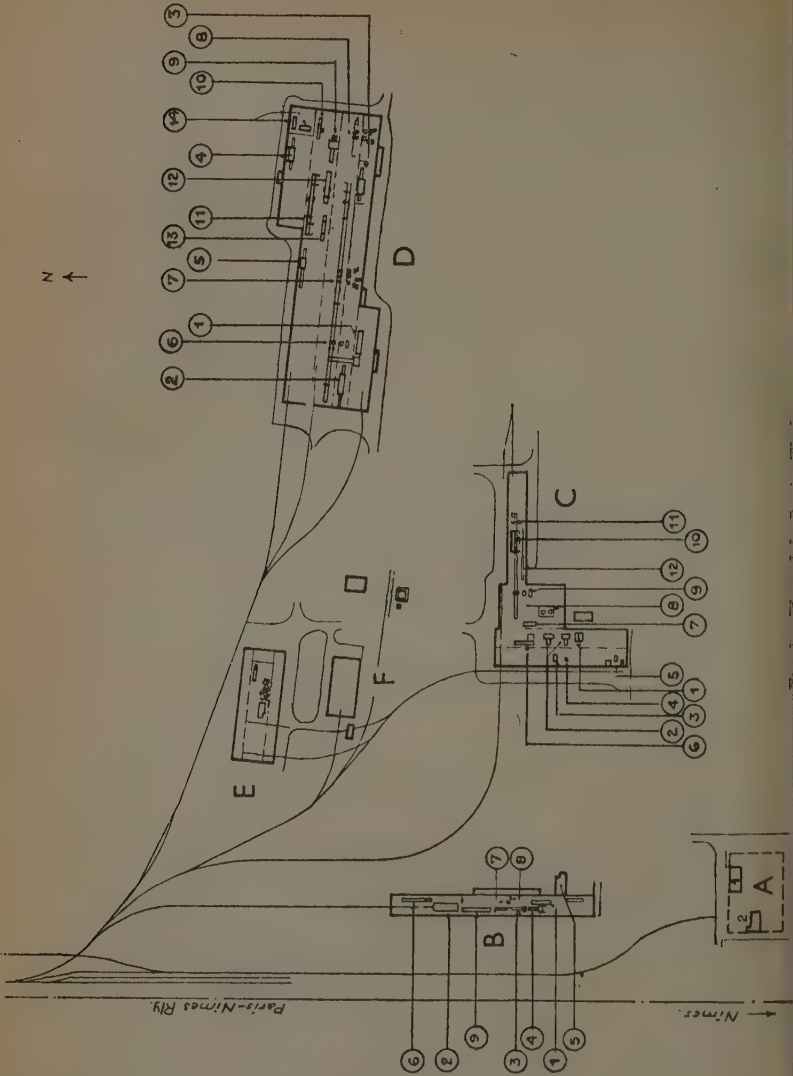
The original 1940 plans also provided for a slabbing mill for the first roughing operations on the slabs for sheet and strip rolling.

(2) *The Rod and Sections Department*, which houses both a 6000-ton extrusion press and rod-rolling mills, with a common shop for the finishing operations, heat-treatment, and quenching plant; equipment for cutting to length and scalping; and an inspection and despatch department.

(3) *The Sheet and Strip-Rolling Department*, containing all the plant necessary for the production of sheet and strip from the pre-heating stage to inspection and despatch.

The rest of the works comprises a transforming and distributing station for electric power; a maintenance shop, equipped for both electrical and mechanical engineering operations, which is located at the centre, roughly equi-distant from the three main departments; a water supply tower and pumping station; offices, stores, laboratory, first-aid post, &c. A plan showing the lay-out is given in Fig. 1.

In spite of the fact that the rod-rolling and section-rolling mill trains were dropped from the plans, the blooming mill built in 1940 was retained, but will not come into proper service until rod- and section-rolling operations are catered for by a complete mill train.



KEY.

A. Electric Power Transformation and Distributing Plant.

1. 26,500 kVA. transformers.
2. Distributing plant.

B. Extrusion Shop.

1. Ingot preheating furnace.
2. Heat-treatment furnace.
3. Preheating furnace for press tools.
4. 6000-ton press.
5. Air-hydraulic accumulator.
6. 350-ton stretching machine.
7. Roller straightening machine.
8. 400-ton vertical press.
9. Quenching trough.

C. The Foundry and Blooming Plant.

Foundry :

1. Oil-fired furnace.
2. Resistance furnace.
3. Induction furnace for melting scrap.
4. Furnace for hardener alloys.
5. Furnace for magnesium.
6. Circular saws.
7. Scalping machine.

Blooming Plant :

8. Pit furnaces.
9. Mill with rolls 1100 mm. in dia. and face width of 2500 mm.
10. Quenching trough.
11. Saws.
12. Scalping machine for ingots.

D. Sheet Rolling Shop.

1. Pit furnaces.
2. Intermediate preheating furnaces.
3. Annealing furnace for coils.
4. Heat-treatment furnace.
5. Continuous annealing furnace for sheet.
6. Reversible rolling mill for slabs, with rolls 2840 mm. wide.
7. Three-stand tandem mill for hot rolling.
8. Two-stand tandem mill for cold rolling.
9. Flying shears.
10. Slitting shears.
11. Shearing line for thick strip.
12. Shearing line for thin strip.
13. 750-ton stretching machine.
14. Rectifiers.

E. Maintenance Shops.

F. Store.

III.—DETAILED DESCRIPTION OF THE PLANT.

1. *The Foundry and Blooming Plant.*

This is made up of four principal shops :

- (a) The metal store, with equipment for remelting small scrap (chips and swarf).
- (b) The casting shop proper, with plant for melting and pouring.
- (c) Sawing and scalping plant for preparing the ingots.
- (d) The blooming mill.

(a) *The Metal Store.*

This is housed in a building 20 m. wide by 135 m. long. It is equipped with wooden racks to stack ingots of aluminium derived from various sources and various metals and alloys.

The charges for the melting furnaces are made up by weighing the components separately and then feeding them into metal channels, fitted with electrically operated charging gear. The shop is equipped with a 250-kW. Ajax-Tama induction furnace which can handle 500 kg. of metal/hr. and which is chiefly used for melting down scalplings, sawings, chips, swarf, and other small waste.

(b) *The Casting Shop Proper.*

This shop is parallel to, and opens out of, the metal store, and is of the same size. The original plans in 1939 catered for the installation of twenty electric resistance furnaces, but only two have actually been installed. The furnaces, supplied by Gautschi of Kreuzlingen, have two separate compartments :

(i) The melting chamber proper, consisting of a 700-kW. electric resistance furnace capable of melting a 5-ton * charge. When the metal is molten it is transferred to :

(ii) a holding furnace, or casting furnace, which is also an electric resistance furnace but of 120 kW. rating. Its capacity is the same as that of the melting furnace, i.e. it takes a 5-ton charge.

A photograph of the furnaces is shown in Fig. 2, Plate CXVI. Both furnaces are of the tilting type, with screw gear, by means of which the melting furnace can be tilted to empty its contents into the holding furnace, while the latter can also be tilted to fill the moulds which are placed directly underneath it. Casting is carried out by the so-called "semi-continuous" method, which is now well known throughout the light alloy industry. It consists in casting the metal in shallow

* All units quoted are metric, including h.p. which = 0.9863 English h.p.

moulds cooled externally with a copious supply of water. At the commencement of casting the mould is closed at the bottom by a piston; when the moulds are full the piston, under hydraulic or mechanical pressure, descends at a rate commensurate with the speed of solidification of the metal. By changing the size of the mould and the piston, different ingot sizes can be produced. The Issoire casting unit can turn out either two square ingots (side 400 or 500 mm.) or two rectangular slabs (200×1100 mm.) more than 7 m. in length (see Fig. 3, Plate CXVI).

By the time the first two electric-furnace units had been installed, the restrictions on the use of electricity in France and the economic factors (price per kWh.) led to the abandonment of electric furnaces for melting. Contact was therefore established with the Établissements Heurtey of Paris to carry out investigations on fuel-oil-fired furnaces. The furnace at present under construction is of a stationary type consisting of:

(i) a melting chamber with a capacity of roughly 13 tons, heated by two heavy-oil burners;

(ii) adjacent to the melting chamber a holding furnace of 6–7 tons capacity, which is also heated by two burners designed to maintain a steady metal temperature.

When the metal is melted in the first chamber a connecting channel is used to transfer about half of it to the holding compartment. During the period of casting the metal from this second compartment into moulds of the type described previously, a new complementary charge is being melted in the first compartment.

(c) *The Sawing and Scalping Plant.*

This is situated at the northern extremity of the foundry building. After casting, the ingots are transferred by an overhead travelling crane to the feed platform of a circular saw. This, having a blade 1.9 m. in dia., has a cutting speed of 1000 m./min. with variable feed ranging between 150 and 1500 mm./min. It can, for example, cut through a 300-mm.-dia. round billet in 27 sec. A photograph appears in Fig. 4 (Plate CXVII).

The ingots cast in the foundry are of three different types:

(1) Rectangular slabs of maximum cross-section 300×1100 mm. for the production of sheet and strip.

(2) Round billets, solid or hollow, of 300-, 400-, or 500-mm. external dia. for the extrusion press.

(3) Square ingots, 400×400 mm. or 500×500 mm., for the rolling of rod stock, which go for roughing on the blooming mill.

All these ingots require scalping after casting, the round billets being handled on a lathe and the rectangular slabs and square ingots on a milling machine in which the ingot is on a moving table and the diameter of the cutter is larger than the width of the surface being scalped.

(d) *The Blooming Mill.*

Square-section ingots, roughly 2 m. in length, are removed after scalping by a scissor-type grip capable of handling ingots weighing up to 3 tons, and are transferred to the preheating furnaces. These are electrically heated and are of the circular pit-type operating on the forced-air-circulation principle. They are housed in a shop parallel to and opening out of the foundry proper. The transformers and control boards for the furnaces are placed at the southern end of the shop, and at the northern end lies the feed table of the blooming mill, to which the pre-heated ingot from the pit furnace is transferred by means of the scissor-type grip.

At the present time there are two of these pit furnaces, each capable of handling up to 20 tons of ingot metal. The furnace performance is such that the metal undergoes soaking (homogenization) at a temperature of 485° – 490° C., depending on the alloy concerned, after which it is allowed to cool slowly down to the rolling temperature; the latter, again depending on the alloy involved, is generally in the neighbourhood of 400° C. The rating of each of these furnaces is 400 kW. The total duration of preheating is in the region of 24 hr., with a maximum consumption of 300 kWh./ton.

The roller tables in front of and behind the blooming mill are arranged at right angles to the length of the preceding shops. The mill proper is housed, together with its motor and electric gear, its control board, transformers and Ilgner set, in a shop which runs parallel to the pit-furnace room. The exit roller table of the mill is arranged in a shop, 23 m. in width and 116 m. long, which is at right angles to the pit-furnace room.

The actual blooming mill, which is of German construction and was originally built in 1920, has been rebuilt and modernized by Delattre et Frouard at Ferrière (see Fig. 5, Plate CXVII). It is a two-high reversing-type mill with rolls 1100 mm. in dia. and a face width of 2500 mm. It can take square ingots of either 400 mm. or 500 mm. side, and reduce these to a minimum section of 110×110 mm., which allows

for scalping to yield blooms 100×100 mm. This rolling is carried out with channelled rolls as is the usual practice.

The mill is driven by a reversible D.C. motor with variable speed control allowing for 0-45 r.p.m. at constant torque and 45-80 r.p.m. at constant power. At constant torque the maximum torque is 260 tons/m., giving at 45 r.p.m. a maximum starting power of 16,300 h.p. The motor is supplied with D.C. at a voltage between 0 and ± 1200 V. by means of an Ilgner set, comprising an asynchronous motor of 5000 V., 50 cycles, 4500 kW. capacity, driving two 2250-kW. generators, each provided with a 42-ton flywheel to supply energy at the moment the ingot enters the mill and avoid excessive demand on the motor. The whole of this mill arrangement conforms to standard practice in steel blooming mills.

At the exit of the blooming mill, a roller table carries the bloom into a quenching trough, from which it is conveyed mechanically to the saw, where the final blooms are cut to length in readiness for their ultimate use as the stock for the rod-rolling and section-rolling mills.

The scalping of the finished blooms is carried out on a special milling machine which can undertake the milling of the four faces of blooms ranging from 300×300 mm. down to a minimum of 100×100 mm., in two operations. The first operation deals with two parallel faces and trues two opposite angles; automatic devices then turn the bloom through 90° to complete the milling of the two remaining faces and the trueing of the other two angles. This machine, which was designed and built by the Établissements C.W.B. of Paris, can deal with three 1.5-m.-long blooms simultaneously.

2. *The Extrusion Shop.*

This shop, originally designed for the extrusion and rod- and section-rolling division, is only partially complete at the present time, and consists of that part of the building necessary to house the 6000-ton extrusion press, its gear, and its auxiliary plant (see Figs. 6 and 7, Plate CXVIII). It consists of one hall measuring 211.5 m. The pre-heating furnace is situated on the southern side, near the entrance. This is an electric furnace of forced-air-circulation type and of 675 kW. rating, comprising five zones of 135 kW. each, with a 25-h.p. air-circulating blower in each zone. The furnace was built by the Salem Engineering Co., of Salem, Ohio.

The billets are loaded longitudinally on six parallel conveyors which can be used separately or simultaneously, giving an output of 2 tons/hr. of billets preheated to 460° C. The billets are conveyed

directly from the furnace to a hoist between the ram and the container of the extrusion press.

The latter is a 6000-ton press built by the Loewy Engineering Co. of Bournemouth. It has a hydraulic feed and operates at a pressure of 300 atm. The hydraulic feed is derived from an air-hydraulic accumulator consisting of four water cylinders of a total content of 1500 l., and twenty air cylinders, the accumulator being supplied with water by two 3-cylinder reciprocating pumps operating at 300 l./min., each driven by a 300-h.p. motor. The press can either turn out tubes starting from hollow billets by bringing into operation a mandrel inside the ram, or can produce rod and sections.

At the exit end of the press, after the usual shearing and sawing to remove the billet end, the section is conveyed on roller conveyors either to the heat-treatment furnaces or, *via* a transfer table and by-passing the heat-treatment furnaces, directly to the finishing operations of straightening, sawing to length, inspection, and despatch.

If the rod requires heat-treatment, a second transfer table deals with it on its exit from the furnace and puts it into the finishing-procedure circuit.

The heat-treatment furnace is of the horizontal type and was also built by the Salem Engineering Co. It is designed for electrical heating on the forced-air-circulation principle and has a rating of 1200 kW. It comprises eight heating zones each of 150 kW. The temperature can be regulated independently in each zone and is thermostatically maintained. The rod or section to be heat-treated enters the furnace longitudinally on a roller platform. As soon as the rod or section is completely inside the furnace the rollers descend, and the product is carried on chains which are arranged transversely in the furnace. The rate of travel of the chains can be controlled, and is adjusted so that the required temperature is reached when the rod has traversed the whole width of the furnace, which is roughly 3 m. Here a set of rollers ascends and lifts the rod from the chains, carrying it in a longitudinal direction out of the furnace, at the exit of which it is rapidly cooled by high-pressure atomized water sprays. The furnace can handle rod and section stock up to 25 m. long. At the exit of the furnace the stock is again carried by a set of rollers and a transfer table to the stretching machine. The latter, hydraulically driven, was built by Hydro-press Inc. of New York, and is capable of exercising a maximum load of 350 tons on the rod to be straightened. As in the case of the heat-treatment furnace, rod stock up to 25 m. long can be handled. One of the heads of the machine can, if necessary, by bringing into action an electric drive, be made to exert a rotating movement which can

untwist a rod or section which has become "corkscrewed" in the process of extrusion or heat-treatment. An overhead crane with a manually controlled bridge handles the products on the straightening machine and from thence carries them to a roller table which conducts them to the saw for cutting to final length, after which they go to the inspection and despatch department.

3. Rolling Sheet and Strip.

The sheet- and strip-rolling shop is the largest in the works, consisting of three main bays of 300 m. in length :

(i) The rolling-mill shop proper, 23 m. wide, housing the hot and cold rolling-mill trains.

(ii) South of this, and attached to it, the motor room, 18 m. wide, in which are situated all the motors, transformers, rectifiers, and all the electric controls for the mills and their auxiliary plant.

(iii) North of the rolling-mill shop proper and parallel and contiguous to it, the finishing shop, 27 m. wide, which contains all the heat-treatment plant, the trueing and straightening plant, shears, &c., and also the inspection and packing departments.

Adjoining these three principal bays, south of the motor room and stretching from its western end, is a small parallel shop, 18 m. wide and 108 m. long, which is known as the furnace room, and contains the pit furnaces for pre-heating the alloy rolling slabs as they come from the foundry. The buildings of this department include another parallel shop 27 m. wide and 120 m. long, situated north of the finishing shop, which contains the heat-treatment furnaces for the sheet. The roll-grinding machinery is at the eastern end, which is partitioned off from the rest of the shop. This building, the first to be erected in the works, and commenced in January 1940, is constructed entirely of reinforced concrete. It had been designed in the year in question, to the specification of the Armement français, to support a 1.5 m.-thick concrete roof, thus being bomb-proof in air raids. The size of the main struts and vertical columns required to carry this bomb-proof structure and the whole style of the building, including its height and its terraced roof, are original, and remain a monument to the French architect, Auguste Perret, who designed it : in appearance it resembles more an ancient temple than a modern industrial building. The total covered surface in this building is in the region of 25,000 m.²

The following paragraphs contain a general description of the plant housed in this division, the order being that followed by the cast slab after it leaves the foundry on its journey through the works until it is

despatched in the form of sheet or strip. A more detailed account of the individual plant follows in Section 4.

The rolling slabs vary in size according to the alloy or the requirements as follows:

thickness from	200 to	300 mm.
width	„	800 „ 1100 mm.
length	„	2000 „ 2500 mm.

The slabs are transported from the foundry on trucks and are stacked in the small south-western shop described above. A 3-ton scissor-type grip handles the ingots and places them vertically in the electric preheating intermediate furnace.

When the necessary temperature is attained the ingots are removed from the furnace by the same scissor grips and are placed on a conveyor which, passing through the machine shop, carries the slab on to the actual table of the hot roughing mill. This mill, situated on the western side of the rolling-mill shop, is a four-high reversing mill with rolls 2840 mm. wide, which in a series of passes reduces the thickness of the slab from its initial 200–300 mm. thickness down to some 15 mm. (see Fig. 8, Plate CXIX). It is possible, if necessary, to stop the rolling process at an intermediate thickness, 60 or 80 mm., in order to give the slab intermediate annealing. If this is to be done, the slab, fed back by the rolls on to the front table of the reversing mill, can first be sheared at both ends by a special shearing machine which can cut through metal up to 90 mm. thick, after which the cut slabs by-pass this shearing machine on an extension of the roller table and are taken up on a conveyor which deposits them on the entry platform of a continuous electric annealing furnace of 3200 kW. rating. A second conveyor takes the hot slab from the exit of the furnace and replaces it on the roller table on the ingoing side of the roughing mill.

When the roughing operations have reduced the thickness to 10–20 mm. according to requirements (on an average 15 mm.) a 60 m.-long “live” roller table carries the strip directly to the hot-rolling tandem mill of the three-stand type, which has also a roll width of 2840 mm. The product is given three successive reductions in this mill to arrive at the final thickness, of the order of 3 mm. Between the hot reversing mill and the hot three-stand tandem mill and incorporated in the roller table, are a guillotine shears and an edge shearing machine which trim the end of the strip and cut it to width before it enters the tandem mill. On the delivery side of the tandem mill a “live” roller table 100 m. long carries the strip to a roll-type coiler with three rolls, on which it is wound into coils to facilitate handling and future rolling in the cold mill.

As they leave the hot mill the coils may be annealed in an annealing furnace (dual-heating type, employing electricity or alternative heavy-oil firing) and after slow cooling in the furnace and afterwards in air, go forward for cold rolling. The latter operation is carried out on a two-high tandem mill with rolls also 2840 mm. wide, situated at the eastern end of the rolling bay.

The cold-rolled strip is carried on conveyors into the adjoining machine shop, where a flying shears, of the Hallden type, cuts it into sheets of up to 10 m. length. This sheet can then be annealed in a forced-air-circulation 1600-kW. electric furnace and subsequently quenched. It is next levelled and sheared on one or other of the two shearing lines installed which include roller levellers, edge shears, and shears for cutting to length, one of the lines being for thick sheet up to 14 mm. in thickness and the other for thin sheet. A 750-ton stretching machine is available for handling sheets 2.4 m. wide and 10 m. long, while a continuous annealing furnace is used when sheet is required for delivery in the annealed condition.

After passing through the various finishing operations the sheets go to the inspection and despatch department which is situated at the western extremity of the machine shop.

In order to give a more exact idea of the route followed by the products in the course of manufacture, this can be summarized by saying that the slab on entering the western wing of the building traverses first the small furnace room, then enters the rolling division to the right of the reversing mill at the western end of this bay, passes through the bay, enters the finishing shop at the eastern end and goes out at the western end of the same shop in the form of the finished product, after a U-shaped journey with the strokes of the U representing a length of 300 m.

4. Details of the Rolling Plant.

(a) Preheating Furnaces.

The furnaces in which the slabs are preheated before hot rolling are rectangular ones of the pit type provided with forced-air circulation and electric heating. Each furnace is of 1000 kW. rating, and the forced-air circulation is provided by a 250-kW. blower. Each of the furnaces, which were built by the *Établissement Heurtey* of Paris, is capable of taking twelve slabs 200 mm. thick or nine slabs 300 mm. thick. The slabs are arranged vertically in the furnaces with a space between them to allow room for gripping by the scissor grip when depositing them in, or removing them from, the furnace. These furnaces give the slabs a soaking treatment at a maximum temperature of 500° C.

The intermediate preheating furnace is a tunnel furnace, also built by the Établissements Heurtey, which is used for the continuous annealing of the products from the roughing mill. These products are carried into the interior of the furnace on four sets of chains which can be handled either together or separately in two groups of two, so that they can be used either two by two for products of less than 1.3 m. in width or together for wider products up to a maximum of 2.6 m. The length of the furnace is 24 m. It is of the forced-air-circulation type with electric heating. Its rating is 3200 kW. distributed between eight zones, and the forced circulation is provided for by eight 60-h.p. blowers; full temperature control is available for each zone.

(b) *Rolling-Mill Train.*

The hot rolling-mill train comprises :

(i) A hot four-high reversing mill with rolls 2840 mm. wide built jointly by the two French firms Chavanne-Brun and Delattre et Frouard to the plans of the United Engineering and Foundry Company, of Pittsburgh.

(ii) A three-stand four-high tandem mill.

The four-high reversing mill has working rolls of 700 mm. in diameter and backing-up rolls of 1370 mm. Both the working and backing rolls are carried on S.K.F. roller bearings, and each of the housings of this mill, which are of cast steel, weighs 115 tons. 75-h.p. motors are provided for opening and closing the rolls at high speeds (800 mm./min.) and 15-h.p. motors for slow speed (38.6 mm./min.).

The actual rolls are driven by a reversing variable-speed motor (two directions 0-50-80 r.p.m.) through a gear box. The motor supplies a constant torque (260 tons/m.) from 0-50 r.p.m. by varying the voltage (D.C. feed, 0-1200 V.) and runs at constant power, 50-80 r.p.m., by varying the excitation. The exciting current is furnished by a separate 220 V. supply. The conventional designs which are usually employed for the control of such large rolling mills furnish the D.C. requisite for the principal motor by means of an Ilgner set, made up of one or more D.C. generators driven by an A.C. motor. The flywheel of high inertia in the motor generator set takes up peak loads resulting from the rolling operation and prevents the total load from falling on the works' grid. The disadvantage of the Ilgner sets is their costliness and the fact that they involve large tonnages of copper and steel in their design. As in the case of all rotating machinery, the outlay on maintenance and replacements involved is also heavy.



FIG. 2.—The Foundry Shop. Showing the two Gautschi furnaces and, beyond them, the oil-fired melting furnaces.



FIG. 3.—The Foundry Shop. The removal of a rolling slab 200 × 1100 mm. and 6 m. in length.

[To face p. 914.]

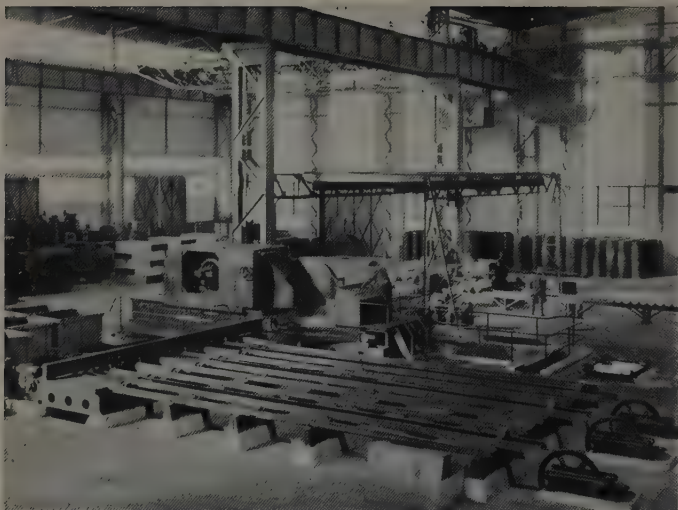


FIG. 4.—The Foundry Shop. The ingot-saw which has a blade 1.9 m. in dia.

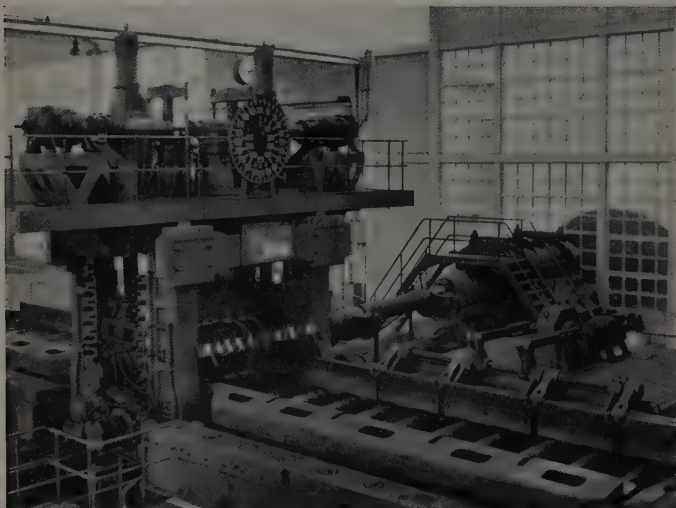


FIG. 5.—The Blooming Mill. The mill and its entrance table.



FIG. 6.—The Extrusion Shop. Showing the 6000-ton extrusion press and its preheating furnace. View from the back of the press.

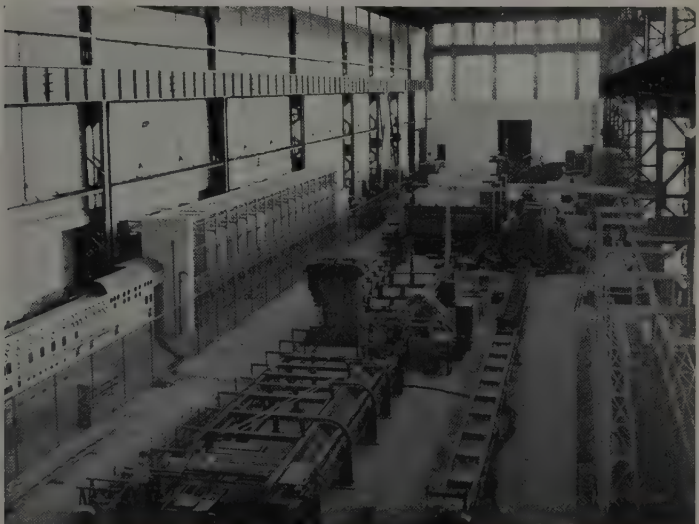


FIG. 7.—The Extrusion Shop. Front view of the press.



FIG. 8.—The Sheet- and Strip-Rolling Shop. The hot-rolling train. In the foreground the 2840 mm.-wide reversing mill. In the background the three-stand tandem mill.

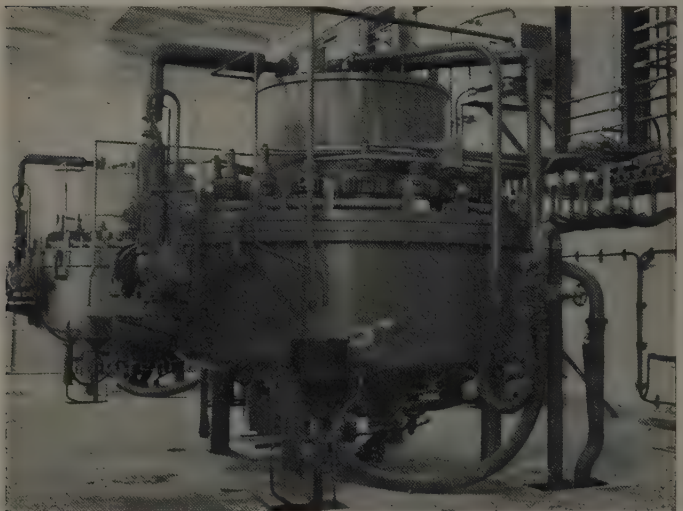


FIG. 9.—The Sheet- and Strip-Rolling Shop. Showing the mercury-vapour rectifiers through the medium of which the reversing-mill is continuously fed.

At Issoire, in place of the standard Ilgner set, the principal motor for the mill is fed through the medium of mercury-vapour rectifiers. An internal works' grid feeds the different shops with 3-phase, 50-cycle supply at 15,000 V. This feeds a set of transformer rectifiers having a total output of 12,000 h.p. (see Fig. 9, Plate OXIX).

Each set consists of a transformer with delta-connected primary windings and three 6-phase star-connected secondaries, supplying an 18-anode mercury-arc rectifier, giving an output of 1200V. D.C.

To start up the mill motor and control the speed between 0 and 50 r.p.m., the rectifier voltage is controlled by means of the grid-regulation system described below.

When the rectifier is brought into action an arc is struck between the graphite anodes and the mercury cathode in the bottom of the rectifier. An auxiliary striking arc, from a separate 220V. D.C. source initiates the arc and results in the passage of current from the anode to the cathode. A grid consisting of a perforated graphite plate is interposed between the anode and cathode, and when negatively polarized by an auxiliary voltage this grid prevents the passage of current. By varying the timing of the application of this auxiliary voltage to the grid, the rectifier is made to conduct for varying proportions of the A.C. input wave, thus giving a variable output voltage which is easily controlled.

The transformer rectifier sets consist of two 3100-kW. rating and one of 2600 kW. They are connected in parallel to feed the reversing-mill motor, or to feed separately the three motors of the tandem train. A reversing switch, which can only function when the D.C. potential is zero, is used to control the direction of rotation of the motor.

The disadvantages of this system are heavy demands of current on the works' grid, and also the power factor of the installation, which is effectively proportional to the voltage.

In front of and behind the mill, machinery is available for turning the blank through 90° so that it may be rolled in the desired direction. Controls are also provided for centring the blanks. Vertical edging rolls, whose speed is synchronized with that of the working rolls, driven by a 400-h.p. motor, control the rolling of the sides of the blank in the roughing passes to keep the width constant. An additional advantage of these edge rolls is that cracking of the edges can be effectively reduced or even entirely prevented.

All the controls for the different movements of the mill are operated from one board situated in a cabin placed at a convenient height on the wall of the rolling-mill bay, so that the operation of the mill is under the complete control of one man.

In front of the mill an extension roller table makes it possible to roll blanks up to 40-45 m. long. Next to this table are placed the shears, which can operate on blanks up to 90 mm. thick and 2840 mm. wide. These shears, designed by the United Engineering and Foundry Company of Pittsburgh, are double-action shears which cut simultaneously with the upper and lower blades. A roller table, 10 m. in length, removes the blanks after shearing, and takes them to the crane which serves the intermediate preheating furnace.

On the other side, next to the working stand of the mill proper, is a long roller table which also receives the blank during the course of rolling and takes it to the guillotine shears which trim the ends of the blank up to 15 mm. thick. These shears are driven by a 100-h.p. motor and are operated from a separate control cabin beside the shears.

A roller table, several metres long, takes over from the previous table and transports the blank to the edging shears which cut the sheet to the required width before it goes to the three-stand hot tandem mill. Roller tables, several metres in length, adjacent to the edging shears, complete the train up to the tandem mill.

This mill is designed with three identical stands, each having four rolls 2840 mm. wide. As in the case of the reversing mill, the working rolls have a dia. of 700 mm. and the backing-up rolls have a dia. of 1370 mm. The housings, in cast steel, each weigh roughly 100 tons. As in the reversing mill, the tandem-mill rolls have S.K.F. roller bearings. The adjustment of the rolls, which in this case run only at one speed, is controlled by two 75-h.p. motors, capable of separate action on each roll-adjusting screw, or of simultaneous operation when a magnetic coupling comes into play. The three stands are as close together as the design of the housing permits. Tables equipped with feed rollers pass the strip continuously from one stand to another. The two first stands are driven by D.C. 4000-h.p., variable-speed (175-350 r.p.m.) motors. The third stand is driven by a 2500-h.p. motor of the same type and with the same speeds. Each of these motors is fed with 1200 volts D.C. by one of the rectifier sets described earlier. In practice, the strip undergoes rolling in the tandem mill directly after leaving the reversing mill, and, since this rolling operation is of very short duration, there is only just time to place the next blank in position on the reversing mill while rolling on the three-stand tandem mill is taking place. It is therefore possible, without appreciable loss of time, to use the rectifier current alternately for one mill train or the other. It will, of course, be possible in the future, if it is desired to increase the output of the hot-mill train, to add a separate supply group for either of these two units.

A pinion stand and speed-reducer are positioned between the principal motor of each mill and the working rolls. These speed-reducers control the maximum rolling speed at the exit side of the last stand at 180 m./min., corresponding to the maximum motor output of 350 r.p.m. and 2500 h.p.; thus the reducer of the third stand has a reduction ratio approximating to $\frac{1}{4.2}$. The reducers of the previous stands have larger reduction ratios, designed so that for the normal working reduction of thickness the speeds of the three motors are effectively equal; which means that in most cases the auxiliary speed-control devices for each motor are little called upon. The entire control of the tandem three-stand mill is undertaken from one control cabin, as in the case of the hot reversing mill.

At the exit side of the tandem mill, a roller table conveys the rolled strip to a guillotine shears to be cut to length, and to an edge shears for cutting to width. On leaving these shears the strip goes to a roll-type coiler of the up-type with three rolls, on which it is formed into coils. One of the bending rolls is designed to move as required closer to or further away from the others, so that the curvature of the turns and the diameter of the coil can be controlled. A swivelling cradle is used to remove the coil and transfer it to an up-ender which turns it into the vertical position so that it may be carried out with the help of an overhead crane. The whole of this plant was built by the United Engineering and Foundry Company.

(c) *Cold-Rolling Mill.*

Cold rolling of strip broken down in this way is carried out on a two-stand, four-high, tandem strip mill, also 2840 mm. wide. The forged-steel work rolls are 620 mm. in dia., while the backing rolls (like those on the breaking-down mill) are 1370 mm. in dia. The cast-steel housings of these mills each weigh 120 tons. The work rolls of each of the two cold mills are driven by a 2500-h.p. variable-speed, D.C. motor (175-350 r.p.m.), through a pinion stand and speed reducer.

At the entrance to the first stand of this tandem train is a levelling device for flattening the end of the strip, which can then be cut off by a small guillotine. The strip is taken up by a small conveyor at ground level, and led into the mill through a feed system comprising a series of rollers in an arrangement similar to a roller-leveller. The strip, after leaving the first stand, passes over a roller equipped with a device to measure the tension in the strip.

On leaving the second stand, the strip is rolled under tension on the drum of a winder. Coiling of strips of thinner gauges is effected by

means of a belt-type wrapper, i.e. by the aid of a belt fitting against the drum of the coiler (which the belt only partly covers), thus holding the strip during the first few turns of the coiler. Thicker strips are attached to the winder by their ends by means of a gripping device. The drum of the winder is driven by two 500-h.p. motors, arranged end to end so that either 500 h.p. or 1000 h.p. can be applied. The second stand of this mill was made by Chavanne-Brun and Delattre, to the American Company's drawings, and the remainder of the equipment was made by the United Engineering and Foundry Company itself.

The various motors of this installation, i.e. the two 2500-h.p. motors of the mills and those of the winder, are fed with D.C. from a group of three rectifiers comprising two of 2100 kW. for the mill-motors and one of 750 kW. for the winder. The output voltage from the rectifiers is adjustable by means of the grid-regulator system described in connection with the hot-rolling mill, thus permitting the desired range of speeds of entry for the strip and its acceleration up to the base motor-speed of 175 r.p.m.; the variation of this from 175 to 350 r.p.m. is obtained by varying the excitation.

(d) *Heat-Treatment Furnaces.*

(i) *Coil Annealing.*—Between hot rolling and cold rolling, the coils can be annealed in dual-heating-type furnaces (electric or oil-fired). The coils are loaded on to platforms carried by driving chains to the furnace entrance and then pass through to the hot zone in which they attain the annealing temperature. After annealing is complete the coils are moved along the furnace by the chains and pass into a second zone in which they are slowly cooled (at an adjustable rate), while a new charge is loaded into the furnace. This furnace, built by the Établissements Heurtey, has an electrical heating rating of 800 kW.

(ii) *Heat-Treatment Furnace.*—This electric furnace, constructed by the General Electric Co. and of 1800 kW. capacity, employs forced convection. It comprises a heating chamber about 4.5 m. high and 11 m. long, supported on stanchions to about 3 m. above floor level, the bottom of the chamber opening over a water-trough sunk in the ground. The charge is loaded through this opening, and is later rapidly lowered through it into the quenching tank. During the heating operation the opening is closed by a sliding door.

The sheets which constitute the charge are hooked to a frame which is led on rails to a position under the furnace, and at the moment of charging it into the furnace or of its descent into the quenching tank the rails move aside to allow the charge to pass.

(iii) *Annealing Furnace for Thin Sheet.*—A dual-heat furnace

(electric and oil-fired) is used for annealing sheets 2.4 m. wide by 10 m. long. This furnace is of conventional type and has no special features requiring description in detail.

(iv) *Finishing Equipment.*—Apart from the Hallden machine, which is larger than equipment of this type as usually designed hitherto, the shearing lines (for thick or thin sheet) are of standard type, i.e. they both have a roller-leveller, edge-shears for cutting to width, and end-guillotines for cutting to length, with an intermediate roller-platform. The Hallden machine was constructed by the United Engineering and Foundry Company and the other shearing machines by Hydro-press Ltd. All are of the conventional familiar design.

The entire rolling-mill assembly, comprising furnaces, rolling-mills, &c., permits the fabrication of thick sheets up to a maximum size of 2400 mm. wide by 10 m. long, and thin sheets of greater length or in very long coils.

5. *General Services.*

The running of such a factory naturally demands a battery of supply services, including among others :

(a) *Power Transformation and Distribution.*

The factory takes electric power (3-phase, 150,000 V., 50 c./s.) from the French grid system near Clermont-Ferrand, 33 km. away. The transformer station has two transformers of open-air type, each of 26,500 kVA., 150,000/15,000 V., while a distributing station provides for the distribution of the 15,000 V. supply to the different departments. In each of these departments, the 15,000 V. supply may be either used direct (e.g. for the transformers of the rectifier sets), or stepped-down further to 380 V. (3-phase) for supplying small motors or to 110 V. for lighting.

(b) *Railways.*

A complete network of rails allows goods trucks arriving at the private siding at Issoire station to be brought to any part of the factory, a Diesel locomotive being used for the purpose.

(c) *Water.*

Wells sunk alongside the river Allier, bounding part of the factory site, are connected by syphon to a pumping station, where two automatic pumps feed a water tower of 800-m.³ capacity placed at the highest point of the factory.

(d) *Maintenance Shops.*

A vast maintenance department, 100 m. long, comprises a central

workshop for the larger machines, together with two side bays—one for the smaller machines, the electrical maintenance services, and the joiners' shop, and the other serving as general stores. This department is fitted with modern machines which, in view of the distance of Issoire from important engineering centres, have to provide for the carrying out of the greater part of even major maintenance work on the factory equipment.

(e) *Offices and Laboratory.*

The managerial and general offices, accounts departments, &c., are at the moment housed in buildings in the maintenance division, but will be later transferred, along with the central chemical and physical control laboratory, to new buildings at the factory entrance. The provisional laboratory facilities comprise a laboratory for chemical and spectrographic analysis and one for mechanical testing. The equipment in this laboratory will moreover be added to in step with the development of the works products.

(f) *First-Aid Post and Dispensary.*

A combined first-aid post and dispensary, with a waiting-room, casualty room, X-ray rooms, &c., provides for accident cases and enables a regular watch to be kept on the health of the personnel.

Finally, there are within the factory site a conference hall, cinema, and theatre for the use of the personnel, and playing fields laid out for basket-ball, tennis, bowls, &c., providing for relaxation outside working hours.

Although, owing to the war, completion of the factory has had to wait more than ten years from the date when it was planned, it can already compete with the most up-to-date factory for the working of light aluminium alloys, since its plant enables it to meet the varied requirements of the market in both price and quality.

SOME TECHNICAL PROBLEMS INFLUENCING PRODUCTION ECONOMY IN THE ROLLING OF ALUMINIUM.*

By W. J. THOMAS, MEMBER,† and W. A. FOWLER, MEMBER.‡

SYNOPSIS.

The world production of rolled aluminium and aluminium alloys has increased four to five times during the last decade. The major part of this additional production has been manufactured in large strip mills calling for heavy slabs and rolling at high speeds. In these mills sheet is produced in coil form and subsequently cut to length. These large mills have introduced economies in production, but there are further potential savings dependent on the satisfactory solution of certain problems which still remain. Some of these problems are inherent in the process and some are relatively new as they are associated with the operation of the modern type of plant.

The paper sets out some of the more technical of these problems by indicating the difficulties which are at present being experienced, the possible causes of these, and some suggestions of what is needed for overcoming them.

The main subjects dealt with are: The casting of large slabs by the semi-continuous method and the difficulties and failures experienced therewith. The reasons for scalping some of these slabs and the economies that would follow its elimination. Rejections due to blister; some of the possible causes of this defect and how it might be avoided. Scrap remelting is an expensive operation, and potential savings would warrant the installation of special equipment. The difficulties and defects experienced in the hot rolling of some of the strong alloys are reviewed, and suggestions are made regarding the reasons for these troubles and means for overcoming them. One of the major problems in the use of modern high-speed strip mills is the cooling and lubrication of the rolls, and the paper reviews the desired properties of the coolant, its application to the rolls, and equipment for filtering and cleaning the rolling oil. The production of rolled metal to intermediate tempers by thermal treatment as against cold working is considered, as with modern rolling plant this method has potential advantages. Means of producing fine-grained metal to facilitate subsequent manufacture are also reviewed. Finally, as modern mills roll sheet in coil form, a case is made for a process and plant to permit of continuous heat-treatment before the coils are cut to length.

The satisfactory solution of the problems referred to will only be achieved by the closest collaboration between production, engineering, and scientific staffs.

I.—INTRODUCTION.

No apology is made for introducing economies into the Proceedings of this learned Society, as sooner or later the economic condition of an industry reflects the initiative and ability of the scientific and technical workers

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in that industry. Other factors obviously have their influence, and these may even be predominant, but the final stream-lining of production procedure in modern manufacturing processes is dependent on the solution of scientific and technical problems.

In the selling price of primary metals the position of aluminium is unique, as in Great Britain and some other large consumer countries the present price is substantially the same as before the recent war, despite the big increase in wages and cost of materials and services.

This is due to the enormous demand created by the war and to meet which very large and, in some cases, completely integrated plants were developed; the size alone of these plants brought about many savings in production costs. At the same time there have been a number of improvements in plant and processes which have resulted in further savings in labour costs and reduced the consumption of electricity, fuel, &c.

On the fabricating side the developments have not been so spectacular, in spite of the fact that the world output of rolled aluminium and aluminium alloys has increased four to five times during the last decade. That some progress has been made, however, is established by the fact that the selling prices of fabricated material—particularly rolled products—have not increased in proportion to the increased cost of labour, stores, and services. The end has, however, by no means been reached of the economies which might be effected.

The savings which have been made, resulting in a selling price lower than would have been possible if the full increases in cost of labour, &c., had to be absorbed, were brought about very largely by the installation of big or continuous or semi-continuous rolling mills, in which large sheet as well as strip is rolled in coil form and subsequently cut to finished length. There is nothing novel in this method of sheet production, as nearly thirty years ago the British Aluminium Company installed a number of mills rolling sheet in coil form up to 3 ft. 6 in. wide. The weight of these coils, however, was only between 300 and 400 lb.; the mills had a maximum rolling speed of 70 ft./min. and were used chiefly for the production of thin sheets in pure aluminium. The modern mills roll coils up to 6 ft. wide and over a ton in weight, at speeds from 500 ft. to more than 1000 ft./min., and as well as rolling pure aluminium they can deal with the stronger alloys up to quite thick gauges.

These modern mills were installed chiefly to meet war-time requirements, when products were much more standardized and bulk production was possible. These conditions do not yet obtain in regard to most commercial requirements, and so full advantage cannot be taken of this new type of plant.

It is not proposed to deal with production-planning problems other

than to say that the light alloy rolling industry in Europe is still mainly a jobbing industry, despite the new production facilities. There is much to be done in encouraging standard sizes so that programme rolling can be developed, and there is certainly considerable scope for reducing the innumerable official and other specifications called for.

The operation of these new plants has brought a series of new problems, and the purpose of this paper is to describe some of the technical problems, the solution of which would permit of further economies that would be to the benefit of the industry and of consumers. In addition to these new operating difficulties, consumers are calling for improvements in physical properties and finish, and they generally require material equal in every respect to that which they were accustomed to receive previously from the slower and more expensive production units. In some cases they are, indeed, more critical, owing to the growing use of pressing in place of spinning, as they are anxious to reduce their own production costs by speeding up their operations. Some of these requirements are at present difficult to obtain in the modern mills and a number of products still have to be manufactured on the older types of plant at higher cost. Therefore, technical developments which would permit of their manufacture on a bulk-production basis would enable economies to be effected which would further stimulate the demand.

Additional continuous or semi-continuous mills are being installed in a number of countries, and thus in many cases there are common problems. The economic solution of some of the difficulties mentioned in this paper is a challenge to the ingenuity and enterprise of all concerned.

Needless to say, the views expressed in this paper are largely based on the experience and research of the British Aluminium Company.

II.—CASTING.

To derive the maximum benefit from the modern rolling process calls for very large rolling slabs, and it is in meeting this requirement that semi-continuous casting has shown to considerable advantage over permanent-mould chill casting. Apart from this, the semi-continuous method has given other advantages, such as permitting simultaneous casting of several slabs, with consequent high output rates, giving generally sounder metal and, with some exceptions, finer grain, eliminating the costly hand feeding necessary with chill casting, and giving greater flexibility in producing a wide range of slab sizes.

The semi-continuous casting method has been widely reviewed in the literature. Briefly, the process consists of pouring metal at a constant rate into a shallow water-cooled mould whose base is moved downwards

at a constant speed to maintain constant metal level in the mould, the emerging slab being also water cooled.

Although in the case of aluminium of normal commercial purity there appears to be no dimensional limit to the size of slab which can be satisfactorily cast, provided a reasonable width:thickness ratio is maintained, certain alloys are much more restricted in this respect. Table I shows some of the larger sizes which are regularly produced.

TABLE I.

Alloys	Slab Thickness, in.	Maximum Width, in.
Pure aluminium	8	48
1.25%-manganese alloy		
2.25%-magnesium alloy		
3.5%-magnesium alloy		
D.T.D. 479R	8	30
D.T.D. 603B		
D.T.D. 390		
D.T.D. 687		
	8	26

Even within the limiting sizes mentioned, casting or hot-rolling difficulties in the form of failures due to cracking or splitting do sometimes occur with the heat-treatable alloys mentioned above, and also with the binary aluminium-magnesium alloys having a relatively high magnesium content. The solution of these difficulties, whose occurrence is generally of an epidemic nature, has yet to be found.

It is appreciated, of course, that by reason of the drastic quenching taking place during casting, very high internal stresses are developed. When the metal is relatively ductile, as with pure aluminium and 1.25%-manganese alloy, the problems are few and the largest slabs can be cast with ease, but with the strong alloys mentioned these internal stresses may lead to serious scrappage on account of cracking. A good deal is known of the mechanism of these stress failures, and it is thought that the residual stresses in the slab may be of varying magnitude with surfaces in tension and centre in compression, or *vice versa*. If the stresses are high enough in either case, then cracked slabs will result, though the type of crack is different for the two systems. The magnitude and type of stress system is determined by a number of factors, such as alloy composition and properties, dimensional proportions of the slab, metal depth in the mould, metal temperature, casting speed, and the amount, uniformity, and position of the application of the coolant.

The aim is to design and maintain casting conditions such that the magnitude of either stress system is kept within certain limits.

Control of the casting conditions mentioned does usually give the desired result, but occasions arise when one alloy, differing even very slightly in composition from another, may cast with notably greater or less ease. These circumstances have directed attention to compositional effects, and investigation has shown that copper, sodium, magnesium, silicon, and the magnesium : silicon ratio all have to be controlled to close limits in the difficult alloys. D.T.D. 687 is the most difficult, while in the Duralumin group D.T.D. 390 can be troublesome.

When the demands of the rolling mills for a heavier slab make it necessary to increase the width, casting of the difficult alloys becomes increasingly critical, and at present there appears to be a definite limit in the width : thickness ratio which can be employed successfully.

Large slabs in a difficult alloy of a given size will be cast under the designed optimum conditions sometimes for weeks at a time, with no sign of trouble, and then quite suddenly a group of stress failures will occur, persisting in spite of all remedial measures, and then the trouble will clear itself for no apparent reason. These epidemics can occur with no observable change in casting conditions or metal composition.

This suggests a change in the metal characteristics, but what these are is something not shown by normal analysis. It may be that cavities, perhaps due to abnormally high gas content and oxide inclusions, weaken the resistance of the slab to the stresses that are put upon it. Investigation of this suggested metal factor is urgently necessary, and also further fundamental work is called for to explain fully the difference in the behaviour of one alloy as compared with another.

III.—SLAB SCALPING.

A characteristic of the semi-continuous method of casting is the presence of regular surface exudations of segregate, sometimes called "blebs", which may in the case of commercial-purity aluminium contain up to 1·8% iron with perhaps 1-2% silicon; in copper-containing alloys the blebs may contain as much as 30% copper.

The blebs are removed by machining or scalping, which in itself is a costly operation involving the installation of expensive machinery. Apart from the actual cost of scalping, the recovery of the swarf is a troublesome and expensive matter. This will be apparent when it is mentioned that scalping swarf amounts to some 5-6% of the weight of the slab, and in remelting this a high loss is experienced.

In the case of strong alloys it is unlikely that scalping can ever be omitted, particularly those requiring cladding. The exudations of segregate are brittle, and if not removed would crack and break up in

rolling, would be inimical to adhesion in those alloys which have to be clad, and would probably lead to excessive diffusion into the protective cladding envelope in later processing. The corrosion-resistance of the finished sheet would certainly be reduced. With these strong alloys, however, it is unlikely that slabs produced by semi-continuous casting are at a disadvantage as compared with slabs produced by chill casting.

In the case of pure aluminium, however, the aim should be to eliminate scalping and thus effect considerable economies in production costs. The one factor which seems to have had the greatest direct effect on the quality of the cast surface is the casting speed, the higher the speed the smoother the resultant surface. It has been found possible to obviate the need for scalping in the case of small slabs in pure aluminium by increasing the casting speed sufficiently.

With the bigger slabs, however, there is a smaller ratio of perimeter area available for cooling to the volume of metal requiring to be cooled, and it has not hitherto been practicable to extract the extra amount of heat sufficiently quickly to permit of maintaining a high speed of drop, and with slabs over 8 in. thick it is difficult to cast at a high enough speed to avoid bleb formation.

Various factors have been tried out in relation to the depth of metal in the mould, design, thickness, and material of the mould, and methods of applying the cooling water. A certain amount of success has been achieved, but so far the bigger slabs cannot be produced with a sufficiently clean surface to avoid the need for scalping or dressing in some way. The successful solution of this problem would effect very considerable economies.

As an indication of the importance of this problem, it can be shown that the cost of scalping and remelting swarf, with the resultant metal loss, can be as high as half the total cost of casting—so that although these large slabs do provide economies at the later stage of rolling, they start at a distinct disadvantage.

IV.—BLISTER.

Rejection for blister has been a problem in the industry since its inception, and, to a varying extent, still remains so.

Although it is possible to produce pure aluminium and low-strength alloys with a fairly consistently low level of blister, particularly since the adoption of semi-continuous casting, the problem of blister in strong alloys remains a serious matter. While with these alloys a solution seems at times to have been found, and fairly prolonged production runs without serious blister rejections can be obtained, sooner or later these

trouble-free runs are brought to an end without any recognizable change in procedure, alloy constitution, or treatment of the metal. On such occasions the application of remedial measures, suggested by past experience as being efficacious, do not always readily cure the trouble. In the past the tendency has been to attack the problem by exploring, rather on a trial-and-error basis, all the many production variables, but latterly the approach has been in the direction of determining the fundamental conditions scientifically, and of applying the knowledge thereby gained, and there is some justification for thinking that by this method production conditions will be put on a more controllable basis.

Fundamentally a blister must occur because a cavity containing some gas is present in the metal. At high temperatures, such as obtain in annealing or solution-treatment, the resistance of the metal to deformation is greatly reduced, the gas pressure is increased, and the cavity blows up to visible proportions. The problem is, therefore, to prevent or reduce the formation of such cavities and to eliminate, as far as possible, the gas which occupies them. Rolling slabs may be clad, and in this case it is necessary to consider the very important possibility of discontinuities occurring at the interface between the "core" and the cover metal, in addition to those within the materials themselves.

Apparatus has been developed which enables the gas in even very small blisters to be identified, and investigations have shown that the gas content consists either of (a) pure hydrogen, or (b) a large proportion of nitrogen with varying percentages of hydrogen. Hydrogen is the only gas which is capable of dissolving and diffusing in both liquid and solid aluminium, and a high proportion of blister is due directly to the presence of this gas in the metal. Nitrogen is insoluble, and there seems little doubt that blisters which contain this gas originate from the air trapped in the metal, either in casting or in rolling. The air can be trapped as a result of turbulence in transfer of the molten metal to the mould or, in the case of chill castings, by the breakdown of shrinkage cavities during solidification; any major cracks occurring during rolling, superficial surface cracks, or relatively deep scalping tool marks are liable to be welded over and produce this type of blister, and in clad metal any dirt or grease at the interface is also a source of trouble.

As far as hydrogen is concerned, considerable information has been obtained as to its solubility in the liquid and solid metal and the conditions under which it can come out of solution and diffuse through the metal. In addition, it is now possible to measure the hydrogen content of the metal by the vacuum extraction of quenched samples, and this provides a very valuable approach to the general problem. The gas content of liquid metal can vary very widely, but is usually of the order

of 0.2-0.5 c.c./100 g. Since the solubility in the solid metal is only about 0.04 c.c./100 g. at the melting point compared with 0.69 c.c./100 g. in the liquid at the same temperature, there is a tendency for gas to be thrown out of solution during solidification, and every effort must be made to reduce the dissolved hydrogen to a minimum.

From extensive tests which have been carried out, it would not appear that the type of fuel used in the melting furnaces, whether coke, steam coal, heavy oil, producer gas, or coal gas, has much influence on the hydrogen pick-up. The main source of gas in the metal is considered to be the hydrated oxide present on both ingot and scrap metal, and the oil or grease films usually present on process scrap. Nevertheless, it is considered good practice to control the furnace atmosphere so that there is little or no direct impingement of the flame on the metal, and to run with the flame slightly on the oxidizing side. It is also undoubtedly beneficial to keep metal temperatures as low as possible, and certainly below about 750° C., since pick-up from the furnace atmosphere is important at temperatures higher than this.

From what has been said, it will be clear that gas porosity in the cast slab can only be avoided if either the hydrogen content of the metal is reduced to below the equilibrium solid solubility, or if the casting conditions are such that supersaturation of the solid can take place. The tendency to form gas bubbles during solidification will be influenced by :

- (a) The initial concentration of gas in the liquid.
- (b) The rate of solidification.
- (c) The freezing range of the alloy.
- (d) The number of suitable nuclei present which are capable of initiating the first separation of molecular hydrogen.

If the gas concentration is fairly low and the nucleation of bubbles difficult (i.e. the metal is "clean" and free from oxide particles), the gas will be retained in supersaturated solution in the solid without the formation of porosity. The gas content which can be tolerated in this way will depend upon the rate of freezing and the freezing range of the metal; it is considerably higher in the case of pure metal than it is in alloys with a long freezing range, e.g. Duralumin-type alloys.

Semi-continuous casting is greatly superior to chill-mould casting from the point of view of gas entrapment, owing to the much greater speed of solidification of the metal.

If gas is retained in supersaturated solid solution, it can diffuse into cavities formed by shrinkage or stress cracks, and the casting conditions should aim to avoid these defects.

The two major problems to be overcome are, therefore, to reduce the gas content of the liquid metal to as low a level as possible, and to get

the metal really clean and free from particles which may act as gas nuclei. While some assistance to this end is given by designing the furnace to permit the maximum escape of the dissolved hydrogen by diffusion (i.e. by keeping the metal depth small), by controlling the furnace atmosphere and temperature and by providing some settling time before casting, it seems clear that something more than such control is needed to avoid periodic blister epidemics, particularly with strong alloy, and the problem is still to find a really satisfactory degassing and cleansing agent for treating the molten metal. Various agents have been suggested and are in everyday use, such as nitrogen, nitrogen mixed with certain volatile chlorides (e.g. carbon tetrachloride), hexachlorethane, aluminium chloride, and chlorine gas. The degassing agents which are the simplest to apply, such as nitrogen and hexachlorethane, do not appear to be as effective with these strong alloys as they are with magnesium-free alloys; chlorine appears to offer some advantage, but its use in the casting shop raises a number of difficulties, especially when very large baths of metal have to be treated. Fluxes of the alkali chloride-fluoride types are also difficult to apply and cannot, in any case, be used with strong alloys. There is obviously very considerable scope for further work in this field, not only to acquire the necessary fundamental data, but also to develop methods of degassing and cleansing which will work satisfactorily in production.

Apart from the major problems mentioned, it will be clear from what has already been said that the arrangements for transferring the metal must be so designed as to reduce turbulence to a minimum, since this will inevitably lead to the entry of dross into the mould. This can be done by keeping the linear flow-rate as low as possible, and by the avoidance of abrupt changes of direction and height of the metal stream. It is a further requisite of good-quality metal that rapid freezing with an open solidification front should obtain, and to this extent the semi-continuous method of casting has contributed largely to a reduction in the blister problem. The avoidance of cracks in casting and hot rolling, which, as mentioned above, are contributory factors in the formation of blister, calls for intensive work on the problems of stress failure which are referred to in Section II of this paper. Again, until such time as production technique has been developed so that cracks in the as-cast surface and underlying porosity will not occur, adequate removal of the surface layer by scalping is necessary. Cracking in later processing must also be avoided by careful control of the hot-rolling conditions, including the preheating temperature, the pass intensity, and roll cooling and lubrication, and there is a considerable amount of knowledge yet to be gained on the effect of these factors.

Finally, with clad strong alloys it is of the greatest importance to take extreme care to ensure that absolute "cleanliness" of the interface between "core" and cover plate is obtained. This calls for scalping of the slab without lubricant, or involves a surface cleaning operation after scalping, the cleaning up of the cover plate by scratch brushing or etching, and the prompt application of the plates to the slab in order to reduce the possibility of dust, grit, or other foreign matter being deposited before rolling begins. Even after taking such care in the cladding operation, conditions in the preheating furnace before hot rolling can cause trouble in the form of water vapour from the furnace atmosphere condensing on the interfaces when the cold slab first enters the furnace, since this leads to corrosion and is inimical to good adhesion between cladding and "core". With oil-fired furnaces there is the additional risk of carbonaceous deposits on the interface. These points call for the most careful attention in the design of the preheating furnaces. Another precaution is to turn off the roll coolant during the first one or two welding passes. This requires, if damage to the rolls is to be avoided, both a carefully designed control system for the coolant and thorough drilling of the mill crew.

V.—SCRAP REMELTING.

Anything from 30 to 50% of the metal cast, depending on the alloy being dealt with, appears as scrap during later processing or final inspection, and has to be returned to the melting furnaces for reconversion into useful metal for a variety of purposes. Such scrap can be classified as: (a) that which is baleable, and (b) that which cannot be baled and must be charged loose into the furnace.

The former type of scrap comprises sawing and scalping swarf, cold-strip-mill scrap in the form of end-pieces or part coils, final sheet-shearing scrap, and rejected sheets and coils. The amount of this type of scrap is generally rather more than half the total. The other unbaleable type of scrap comprises parts of rolling slabs arising from casting and hot-rolling failures and end off-cuts, end and edge trimmings from the hot mill, and edge trimmings from the cold mill in small pieces up to 9 in. long. Of the baleable scrap some of the larger sheets and coils have to be cut up into small pieces before they can be baled. This cutting up and the baling operation itself are both very expensive, and call for the provision of additional and costly plant.

These circumstances make the recovery of scrap an expensive matter. In the light of experience during the war with furnaces specially designed for the bulk melting of aeroplane scrap, considerable thought has been

given to the design requirements of a furnace which would permit rolling-mill scrap to be remelted in bulk as received, and without the preparatory processes of cutting up and baling. The design of suitable furnaces for this purpose calls for the closest collaboration between furnace builders and users. Alternative types of furnace have been considered in which scrap would be charged in bulk either direct into the molten bath, or along a preheating chamber before entering the bath. It is envisaged that a bulk charge of scrap, whatever method is adopted, would comprise at least 10 cwt. of material.

While not tried out, it is thought that to deposit such a quantity direct into a molten bath of, say, 10-tons capacity, would not lead to rapid melting of the scrap, and with repeated charges of scrap, some freezing up of the bath might occur. It is also thought that there would be risk of undue splashing, and disturbance and washing in of the oxide film on the metal. Further, as most of the scrap would be oily or greasy, there would be a risk of gas pick-up. The only advantage of this method of charging in bulk would be that the scrap would not be exposed to oxidation, but would be immediately submerged in molten metal, and metal losses might, therefore, be less.

The alternative arrangement that has been considered would comprise a bath of liquid metal of normal capacity, say, 10 tons, the scrap being fed to it over a sloping preheating hearth of about the same length as the bath itself. It is envisaged that the metal would be brought up to a semi-molten state during its passage along the preheating hearth, and that over this period any oil or grease would be burnt off. The furnace would be fired with burners directed to the roof over the bath, with additional burners placed in the preheating zones at a low level to deal with the more solid type of scrap. It is possible that the oxidation loss with such a furnace would be rather on the high side, but this could be kept to a minimum with the adoption of a slightly reducing flame. Several types of charger have been considered, but they are all more or less the same in principle, namely a box or tray holding 10-15 cwt. of scrap pushed hydraulically or by electrically operated screw through the end door of the furnace. The contents of the box could be discharged from it in several ways. There would seem to be no insuperable difficulty at all in devising a satisfactory charging gear. It is possible that the continual pushing of large quantities of scrap along the preheating hearth will cause break-up or erosion of the floor, and lead to fairly heavy maintenance, but the furnace builders should be able to design a satisfactory hearth.

VI.—HOT ROLLING OF STRONG ALLOYS.

The flood-cooling and lubrication of hot mills by a copious supply of soluble oil seems now to be standard practice throughout the light-alloy rolling industry, being essential if high throughput rates such as are demanded from a modern mill are to be achieved. Further, such a cooling system permits complete stability of the mill conditions, without which certain of the stronger alloys in the larger slabs with which we are concerned could not be rolled at all. As is well known, however, some of the stronger alloys are most difficult to roll, perhaps the most troublesome being D.T.D. 687, followed closely by the D.T.D. 390 type.

In extreme cases complete disintegration of the slab can take place, but normally one or more of the following conditions develop:

(a) *Surface Cracking*, which may lead to trouble later in the form of spill or blister.

(b) *Edge Cracking*.—This nearly always develops in strong alloy slabs, as a general fraying of the overlap edges when they are unsupported by metal below, resulting in a saw-like edge on the final blank with serrations up to 2 in. deep. These rough edges have to be completely removed by trimming. Even the smallest crack left in the edge of the main body of the metal may result, in later processing, in breakage of the coil. The hot-rolling edge scrap in the case of strong alloys is quite substantial and can be up to 10% of the original weight of the slab. Considerable expense is entailed in remelting this scrap, and there is the further disadvantage that the unit weight of the piece for later rolling is reduced.

(c) “*Crocodiling*”.—This is in the form of cracking or splitting in a horizontal plane of the leading edge of the slab at the moment of passing through the rolls, the two halves of the slab following the rolls round and opening apart from one another. This may continue for a foot or two, although instances have been known where the crack or split has persisted from end to end of the slab, which has been completely divided into two almost equal slabs of half thickness. Obviously this defect is a serious one, as at the best it slows up rolling and possibly endangers the plant, and entails the creation of scrap in a form difficult to handle. The greatest concern, however, is the possibility of the crocodiling extending into the body of the metal in the form of lamination, and special care is taken to ensure that all traces of lamination are removed by shearing pieces off the end of the blank until sound metal is reached. The supersonic crack detector which has been developed has proved extremely valuable, in production use, in detecting the limits of the affected areas of hot-rolled blanks.

Considerable thought has been given and investigation applied to discovering the causes of these defects and the means for curing them, but it cannot be said that entire success has yet been achieved. While it is known that the larger the slab the greater the difficulties, in this matter it is probably a case of the fundamental causes not yet being fully understood. It is likely that they lie in the original casting process, but hot-rolling conditions can make the difficulties more or less severe.

Crocodiling can be very much reduced by adopting a greater convexity for the edges of the slab and presenting this shaped edge to the rolls. In general, crocodiling occurs, when reducing from an original 8 in. thickness, at 2-3 in. thick, and if the width of the final strip or sheet is sufficient to permit the practice of widening up to this thickness, so that the shaped edges can be presented to the rolls throughout the range from 8 in. to 2-3 in., crocodiling will usually be inhibited.

Recent work has also shown that it is advantageous to increase the amount of convexity of the edges of the cast slabs, from the point of view of reducing edge cracking, it being suspected that insufficient convexity was converted into concavity during the initial hot-rolling stages, causing additional edge cracking during rolling down to the final blank thickness. It is not common practice to scalp the edges of rolling slabs, but it is possible that if this were done there would be an improvement.

There is no doubt that small differences in composition, within the ranges permitted by the various specifications, can have considerable influence on the tendency to edge cracking or crocodiling. For example, magnesium appears to have a very potent effect on edge cracking, while, on the other hand, copper and manganese do not seem to have the same effect. Also of importance in the heat-treatable Dural-type alloys is the magnesium : silicon ratio ; while for these alloys, and also for D.T.D. 687, the presence of sodium is adverse. In regard to the compositional effect on the hot-rolling behaviour of all these alloys, there is probably the same obscure metallurgical factor prevailing as has been mentioned in Section II of the paper dealing with the semi-continuous casting process, in reference to epidemic stress failures.

Maintenance of ductility of the slab is a potent factor with these hard alloys and, in fact, in the case of D.T.D. 687, and sometimes with D.T.D. 390, it is essential to employ two-stage hot rolling. For certain alloys such as D.T.D. 687 it is also necessary to homogenize the metal before hot rolling.

Actual experience in the mill indicates that when a spate of trouble in the form of excessive edge cracking or crocodiling is occurring some immediate relief can be obtained by resorting to lighter passes, but a real solution lies in the casting conditions and/or the slab shape.

It is understood that in America where similar alloys are rolled, benefit has been obtained from the use of edge rollers. These edge rollers work in conjunction with the hot mill, and the slab is given a series of edge-rolling passes during the hot-rolling process. It is thought that the edge rolling breaks down the cast structure and consolidates the edges of the slab and makes them more able to withstand, without failure and cracking, the stresses arising during hot rolling. Certainly some remarkable results have been quoted, it being claimed that edge cracking has been almost, or completely, eliminated, but there seems to be little experience in Great Britain of this practice of edge rolling as applied to light alloys. It entails a very expensive piece of plant which is hard to justify, and the views of the industry on this and all factors associated with edge cracking and crocodiling would be of value.

VII.—ROLL COOLING AND LUBRICATION.

The roll-cooling and lubricating conditions in a modern rolling mill are matters of very considerable importance affecting the economy of production and the quality of the product. On the hot-rolling side substantial progress had been made before the war, but on the cold-rolling side major developments, as far as aluminium rolling is concerned, did not occur until during and since the war, and American practice has had considerable influence on these developments. To achieve the desired results has called for the closest collaboration with the oil companies and their technologists. Not only have they had to interest themselves in and generally understand the production technology of aluminium rolling, but equally those engaged in the rolling industry have had to extend their knowledge to the technology of oils and other lubricants and coolants. While substantial progress has been made, there are still many outstanding problems to be solved.

For the hot rolling of aluminium and its alloys, it is now the general practice to flood the rolls with a copious supply of an emulsion formed by a water-soluble oil at a concentration of 1-2%. While most installations are similar in principle, each case must be carefully considered with particular reference to the type of water available and the soluble oil appropriate to this water, from the point of view of the stability of the emulsion under the rolling conditions. Even when a selection has been made, after careful consideration and trials by both the oil supplier and the user, satisfactory operation can only be obtained by a continuous check on the optimum oil concentration, by the removal by filtration or settlement of liberated oils or entrained grease or dirt, and by close control of the temperature of the solution and the condition of the rolls.

The high outputs in hot rolling now achieved have only been made

possible by the development of satisfactory soluble-oil coolants, and if the system is carefully controlled, good clean blanks can be obtained. It is possible, and indeed essential, so to control the application of the coolant to the roll barrels that the camber of the latter is adjusted to suit the reductions being carried out and to ensure a flat blank shape. The distribution of the coolant over the barrel can be very critical.

A feature of hot rolling aluminium, using the soluble-oil solution as a roll coolant, is that there is a tendency for adhesion between the surface of the slab and that of the roll barrel, which leads to the production of a coating of aluminium and its oxide on the roll. If this coating is completely removed, say, by the use of wire-brush wipers, there is a risk of a fine coating of iron oxide being rolled into the surface of the slab, resulting in a dirty brown appearance, and further, clean smooth rolls cause failure to "bite" and skidding. It is therefore essential to maintain a slight roll coating, and this can be achieved by using wooden wipers preferably maintained in contact with the roll by hydraulic or similar pressure. The aim is to obtain a thin uniform adherent coating of a silky nature. If this is not obtained the coating will build up to an excessive extent and finally flake off and be transferred to the surface of the slab, where it will be rolled in, giving an unsightly appearance persisting right down to the finished sheet. It is therefore important to use a soluble oil of a type and at a concentration which strikes a fine balance between excessive roll coating and a degree of greasiness which leads to skidding. Very minor changes in the oil supplied, in the water used, and in the cleanliness of the system, will upset this balance, and delays and considerable expense may be incurred before the situation is restored. Once having established the requisite conditions, careful control of them should be continuously applied.

Earlier practice has been to limit the hot-rolled finished thickness to approximately 0.25 in., or slightly less, but with the advent of the modern continuous strip mill, in the form of tandem four-high mills installed in line with the hot breaking-down mills, it is now becoming the practice to carry the hot rolling still further on the tandem mills, say, down to 0.1 in. This has obvious advantages, permitting a much greater output in the initial hot rolling stage and in the preparatory stage of finish rolling, but it does introduce a problem to ensure that the hot-rolled strip is sufficiently clean and of satisfactory surface to give the finish required on the final sheets. This might be done either by employing special lubricants on these warm finishing mills or by taking precautions to prevent undue coating of the rolls. The limitation of the coating might be achieved by the introduction of high-speed rotary soft wire brushes applied to the work rolls, but with these there is the risk of

pick-up from the brushes, in the form of finely divided particles, becoming impressed into the sheet. In regard to the alternative of a special lubricant, what seems to be wanted is a non-volatile oil or other lubricant suitable for flood application to the rolls and for working in conjunction with metal at a temperature in the region of 300° C., having adequate lubricating and cooling properties, and which would give a uniform clean surface of good colour on the warm rolled stock.

It is, probably, in the final cold-rolling stages using modern high speed four-high or heavy two-high strip mills, that the greatest developments have occurred in regard to roll cooling and lubrication, but considerable progress still remains to be made. With mills capable of effecting a reduction in a single pass of 50% or more, and at speeds from 400 to 2000 ft./min., the requirements in regard to the dissipation of the heat generated and the lubrication of the roll bite are entirely different from those obtaining with the older type of strip and sheet mills effecting reductions of the order of 5-25% at speeds from 50 to 200 ft./min. Full advantage cannot be taken of the capacity of the modern mills unless very adequate provision is made for roll cooling and lubrication.

In the first stages of development of these mills the usual practice was to employ separate lubricating and cooling systems, the former being by means of a drip feed of a mineral oil, and the latter by internal cooling of the rolls and/or by applying to the roll barrels, cooling boxes or pads containing soluble oil in water, the boxes being sealed against the roll surface. This combination has been found inadequate for the requirements, as the cooling was insufficient to permit the required control of the thermal camber created in the rolls and this restricted the speed and intensity of rolling. Further, both the lubricating medium and the cooling medium—the latter due to leakages—caused staining defects. Latest developments have largely been influenced, as already mentioned, by progress in America, and these are in the direction of applying in a copious flood, by means of sprays, a common lubricant and coolant. The generally favoured medium is a mineral oil suitably "doctored", but there is a possibility that satisfactory results might be obtained by a water-oil emulsion, if this also is suitably "doctored" in order to inhibit staining. However, the most promising approach is in the direction of flood application of a mineral-base oil containing suitable additives. The essential requirements of such an oil are that it should cool and lubricate and also have non-staining properties. In regard to cooling, it has been found that the quantity requiring to be circulated is much greater than if, say, soluble oil and water were used, and it is also necessary to cool the oil very adequately before it reaches the rolls. However, provided sufficient oil is circulated and really ample provision

for cooling is made, the oil will serve as an excellent coolant and, by careful control of the sprays across the roll barrel, will enable the operator to regulate the extent and shape of the thermal camber. To stand up to the extremely high rolling pressures, and to ensure that heavy reductions at high speed can be carried out without damage to the metal or roll surface, and with a reasonable power consumption, calls for an oil of high lubricating value and film strength. Some mineral-base oils possess this quality in themselves, but in other respects are unsuitable, and so far the most promising lubricant has been a light mineral oil blended with additives designed to increase its lubricity, the blend having properties approximating to a Redwood viscosity at 100° F. of 42 sec., and an open flash point of 265° F. (130° C.). The large-scale trials, both in this country and in America, usually indicate that the best results are obtained from the same mineral-base oil, and it is only in regard to the additives that much variation has occurred.

In spite of all precautions, which will be mentioned later, it is practically impossible to ensure that the rolled strip will be free from oil, and as some annealing process will usually follow cold rolling, one of the major difficulties has been to discover an oil which will not leave a stain on annealing. It is in respect of this staining tendency that the heavier mineral oils have been found much worse than the light mineral oil now generally used. This is not to say that the latter gives freedom from staining. Unfortunately, the complete solution of this problem has yet to be found. Tests indicate that it is not the light mineral oil itself which causes the stain, but the additive with which it is blended. The stains may be brownish or iridescent, and can occur sporadically and quite often in narrow zones near the edges of the metal. They can be removed subsequently only by such expensive means as scratch brushing or burning off, and in severe cases, lead to heavy rejections of the finished product. Typical additives are vegetable oils, fatty acids, or organic compounds of phosphorus. It is generally the two former which cause staining, whereas the compounds of phosphorus, while more satisfactory from this point of view, give rise to very objectionable fumes.

Devices adopted at the mill itself to minimize this staining problem by removing surface oil by means of wipers and air jets have not been completely successful. Failing the discovery of a lubricant which will not leave a stain after annealing, the solution may lie in carrying out the latter process in such a way as not to create a stain. Tests have shown that free access of air at a suitable temperature will bring about disappearance of the stain. This latter condition might be obtained by a continuous strip-annealing furnace in which the coil is unwound as the strip passes through the furnace, and rewound after

annealing. Such a furnace would have other applications, and will be dealt with in somewhat greater detail later in this paper (see p. 942). Degreasing has been considered, but such a process is not attractive in view of the volume of metal to be handled, the outputs required, and the capital and working costs that would be involved.

It should be mentioned that the staining problem arises even with new clean oil, and becomes still more serious as the oil gets dirty in use. If no attempt is made to keep the oil clean it acquires, after a week or two, a very dirty black appearance, causing a dull and unattractive finish on the metal and even more objectionable staining after annealing. The oil becomes loaded with finely divided aluminium and aluminium oxide, and a very difficult filtration problem for the removal of this contaminant is presented. It not only spoils the appearance of the finished sheet, but it very much reduces the load-bearing capacity of the oil, and it becomes necessary to decrease the percentage reduction and/or the rolling speed. Again American practice, supplemented by trials in this country, has shown the direction in which to seek a solution of the filtration problem. The most promising method is to carry out a rough filtration or clarification of the whole of the oil in circulation by equipment capable of removing particles down to about $10\ \mu$ size and to by-pass, say, about 30% of the oil in circulation through a fine filtration system using fuller's earth or the like as the filtering medium. Continuous filtration plants of this sort are very expensive, and take up a lot of space, but at present there is no satisfactory alternative to their use. Such a filtration system should be designed to maintain the contaminant in the oil at not more than 0.005 wt.-%.

There is a growing demand for strip-rolled sheets, approximately 0.012 in. thick, for the canning and box-making industries, and frequently consumers require an entirely oil-free material to be supplied. Even the small amount of oil left on the strip with the older methods of rolling by slow-speed mills employing light reductions, is difficult to remove, and the problem is far more serious when the sheets are produced on modern high-speed heavy-reduction strip mills requiring flood lubrication. Efforts have been made to remove the oil by various means, such as by dilution with low-flash-point solvents and physical removal by means of solvent baths, sawdust boxes, wipers, air blowers, and by interleaving with paper as the strip is wound on to the drum. These methods have been used separately and in combination, but have not been entirely satisfactory, even with slow-speed rolling. Some producers follow the rolling process by a degreasing or other chemical process in order to obtain the complete removal of surface traces of oil, but the cost of such additional processes is high in relation to the total rolling cost. There is

a problem here, therefore, for the oil technologist or chemist to overcome. That is, to produce a rolling oil or other lubricant which will meet one of the following alternatives :

(a) It should completely evaporate from the strip after rolling, or by the application of a subsequent low-temperature treatment, or be otherwise completely and cheaply removable, or

(b) if traces do remain on the strip, then the oil or lubricant should be of such a character that it will have no deleterious effect on food containers or on the adhesion of paints or lacquers.

VIII.—TEMPER CONTROL.

Pure aluminium and its non-heat-treatable alloys are produced in sheet and strip form in different "tempers", namely soft, quarter-hard, half-hard, three-quarter-hard, and hard. These tempers are usually obtained by different degrees of strain-hardening; thus, for intermediate tempers the metal is usually given some preliminary cold rolling, is then annealed, i.e. fully softened, and is then further worked by more cold rolling to the finished gauge, the annealing gauge being such that the amount of cold work given to the metal between it and the finished gauge is just sufficient to produce the required properties.

Material to intermediate tempers costs more to produce than either hard or soft material because of the interruption to rolling, and this disadvantage is more pronounced with the large modern high-speed mills which roll in coil form. Further, the most important disadvantage of the interruption caused by the temper anneal is that the final temper reduction is often very much less than the mill is capable of giving; in some cases it may be as small as 10%, and to employ a mill capable of effecting a reduction of 60–70% on this duty is obviously uneconomical. Indeed, in most cases, had the interruption for the temper anneal not been necessary, the mill would have been capable of effecting the complete reduction in one or two passes instead of the two or three respectively that the temper anneal necessitates. A further point is that the wide variations in reductions called for, from very light ones in the case of quarter- and half-hard tempers to heavy ones in the case of soft, three-quarter-hard and hard, leads to trouble because of the wider range of roll cambers and winding tensions needed. It will be realized too that, if the finished properties are to be reasonably consistent, the temper annealing and finished gauges must be quite accurately controlled, a matter of some difficulty in the case of thinner gauges and also with those alloys which work-harden rapidly.

The difficulties mentioned could be eliminated by cold rolling straight

to the finished gauge, and then finally applying a controlled partial-anneal, sometimes called "temper letting down".

When rolled aluminium, or one of its alloys, is heated, its properties change gradually over a period of time, the tensile strength falling to the value for fully annealed material in an interval which may be a matter of seconds at the commonly accepted annealing temperature, or a thousand hours or more at 200° C. At intermediate temperatures the rate of softening is such as to allow the interruption of the process at a point when the desired mechanical properties have been attained. The initial stages of the softening process are unaccompanied by any change in structure detectable by normal means, the change in properties being simply due to the relief of internal strain. If carried on long enough, recrystallization and full softening will occur, but in applying the process it is desirable to ensure that the partial anneal is purely one of strain relief, as partial recrystallization would result in a non-uniform texture.

Such "letting down" processes are quite practicable and consist of heating at low temperatures for a sensible period of time. Low temperature has to be employed because the higher the temperature the more quickly does the process proceed through the stage of strain relaxation to that of recrystallization, and eventually complete annealing, and it is only by the use of a very closely controlled low temperature that the time of treatment becomes less critical. The process also calls for a close control of the temperature at which the original slab was hot rolled. Temper letting down is applicable to pure metal, with the exception perhaps of quarter-hard, as the tensile strength range for this temper involves heating under conditions where recrystallization is likely to occur. The lower tempers, which involve the risk of entering the recrystallization range, are still more impracticable in those alloys prone to become coarse-grained unless heated very rapidly through that range. The process is also usefully applicable to those alloys, for example, the binary magnesium alloys, which work-harden so rapidly as to make property control by the conventional rolling methods difficult. With such alloys the method has the further advantage of giving much less discoloration because of the low temperature employed.

In some cases, quite an important benefit of the temper letting down process is that, compared with temper rolling for a given U.T.S., the former gives a much higher ductility as illustrated by the results on pure half-hard metal shown in Table II.

While the process, as will be seen, is technically very attractive, further work is needed to establish that this method of treatment has definite economic advantages over the strain-hardening process. This

TABLE II.

Temper Rolling		Letting Down	
Mean U.T.S., tons/in. ²	Percentage Elongation on 2 in., Range	Mean U.T.S., tons/in. ²	Percentage Elongation on 2 in., Range
7.3	2.5-7	7.4	17-18
8.2	2 -5	8.1	9-17

will call for a furnace of such design that the total time of thermal treatment and the amount of energy absorbed are kept as low as possible, and that the total cost involved will not exceed that which is necessitated by interrupting rolling procedure and giving a normal anneal.

IX.—GRAIN-SIZE.

Users are demanding finer and finer grain for circles and sheets for deep drawing, so that while a standard of 400 grains/mm.² was sufficient before the war, 800-1000 is not now good enough for many customers. It is imperative that metal in soft or intermediate temper destined for use in any forming operation has a fine grain, not because of any deterioration in mechanical properties associated with an increase in grain-size, but because of the superficial roughness which develops when the metal is subjected to some forms of deformation. To remove the roughness polishing is essential, and this can be a very costly item.

Coarse grain is comparatively rare in commercial-purity aluminium, provided close control is exercised of the metal purity and of the well-known optimum conditions. There is little difference in the final results obtained between the use of semi-continuous-cast and chill-cast rolling slabs, although the former is liable to give trouble with thicker sheets and circles. In regard to the effect of composition, it has been found that to obtain the best results the iron content should not be below 0.4%, with a silicon range of 0.18-0.20%, and the manganese should be kept below 0.02%. Grain refiners such as titanium and boron may help in giving a uniform grain-size. Homogenization is of no particular advantage from the grain-size point of view except, perhaps, in the case of thicker sheets and circles produced from semi-continuous-cast slabs. A rapid rate of heating does give improved results but is not vitally important.

It is with 1.25%-manganese alloy that the greatest difficulty in achieving a fine grain is experienced and in regard to which some problems remain to be solved if economic production is to be obtained.

With this alloy the semi-continuous casting method is at a dis-

advantage with that of chill casting. In regard to composition, the iron content should be kept fairly high, 0.4% being regarded as a minimum. In spite of many efforts it has not been possible to find any grain-refining element which would have a noticeable effect on the grain-size. The addition of small quantities of copper or magnesium does help very slightly but not sufficiently to obviate the need for special processing conditions for this alloy. Homogenizing, i.e. heating for a period of 12 hr. at a temperature of about 570° C., either immediately before or after hot rolling, is essential in the case of semi-continuous-cast metal and also beneficial with chill cast.

It is the annealing conditions which undoubtedly have the greatest influence on the final grain-size of 1.25%-manganese alloy. It is essential, both with chill-cast and semi-continuous-cast metal, even when the latter has been homogenized, to ensure that the recrystallization range is traversed in a matter of seconds which, in effect, means taking the metal from room temperature to the annealing point in a period of 2-3 min. It has not been possible to obtain this so-called "flash" annealing with the conventional type of furnace using heavy and bulky charges such as large tight-wound coils or stacks of flat sheets. It should be remembered that with this alloy the necessity for a flash anneal arises not only for soft-temper sheet and strip, but also, particularly when using semi-continuous-cast metal, for quarter-hard and half-hard tempers. There is well-tried equipment available for the flash annealing of the metal in single flat sheet form, namely a conveyor-type furnace through which single sheets are rapidly passed. There is, however, at present no suitable equipment available for the flash annealing of the metal in coil form. In consequence, with the growing demand for fine-grained intermediate tempers in 1.25%-manganese alloy, the compulsory conversion of the coiled strip into flat sheets at the temper-anneal gauge in order to carry out a flash anneal, raises a serious problem from the point of view of economic production. Instead of being able to roll to finished gauge at the high speeds obtainable on modern strip mills, the producer is obliged to carry out the final rolling on the old type of flat-sheet mill, the rolling rates of which are much less than those which can be achieved on a high-speed strip mill.

Some means of flash annealing continuously in strip form must, therefore, be developed. What is required is a furnace capable of receiving coils of metal, flash annealing the strip while it is paid out from the coils, and then re-winding the metal. Before re-winding, however, in order to avoid surface damage which would occur if the metal were wound hot, the strip should be cooled. Because of the softness and low strength of the metal in the region of the annealing temperature, there

are problems to be overcome of supporting it on its passage through the furnace in such a way that abrasion does not occur, and of re-winding it under a reasonable amount of tension so that the strip will not break or stretch unduly. If the strip were taken through the furnace horizontally on support rolls or on a conveyor, the materials employed for these would have to be carefully selected, and very precise speed-matching would have to be provided to ensure that there would be no relative movement between metal and supports. Alternatively, the flat strip might be allowed to hang freely as a catenary, but this would require special shaping of the furnace chamber and still leave the question of tension and stretch to be solved. Carried to an extreme, the catenary principle could be developed into a vertical furnace, but even with this type there would still be problems to be faced in regard to surface abrasion and tension control and stretch. (It is understood that vertical furnaces have been built in America, but little information is available as to the results obtained, with particular reference to the surface quality of the metal.) The continuous cooling of the metal introduces further difficulties, because if this is carried out by a water quench or spray, as would probably be necessary, there is the problem of removing residual liquid by drying. It seems clear that whatever type of furnace, with associated cooling and drying zones, is provided, a considerable loss of time would occur if each coil had to be threaded through the equipment separately. To be an economic proposition it would be necessary to obtain truly continuous working by welding and stitching the trailing end of one coil on to the leading end of the next, and by providing some means at the outlet end for cutting the strip at the weld or stitch, and then winding up the coils again separately.

In regard to the form of heating that should be applied, it seems that existing and well-tried methods would be suitable, for example, radiant heating and high-speed air-circulation convection heating. In addition, consideration has been given to contact heating by which the metal would pass over and be supported on, say, a heated drum. The possibility of using induction heating has been examined, and this method has attractions in that the heat would be generated in the metal itself; further, it should be possible to get the metal up to temperature over a very short length, say, 2 or 3 ft., and the supporting and tensioning problems would not be quite so serious as in the case of furnaces employing other methods of heating. It is not thought, however, that the way in which the heat is imparted to the metal is a serious problem. Where the difficulties are likely to arise is in providing the mechanical equipment comprising unwinding and winding gear, tensioning apparatus, supporting rollers, welding or stitching machines, shears, &c., all con-

structed, speed-matched, and controlled to ensure that the metal will not be damaged. It is appreciated that somewhat similar equipment has been provided and works successfully for other metals, but there is not the same problem with these in regard to the softness and low strength of the strip during the annealing process, which in the case of aluminium and its manganese alloy render them so liable to suffer surface damage.

Undoubtedly, development on the lines described must occur if full advantage is to be obtained from modern high-speed rolling methods in the production of intermediate tempers in 1.25%-manganese alloy. The continuous flash annealing of wide strip should, therefore, receive the serious attention of furnace builders.

X.—THE HEAT-TREATMENT PROCESS.

It is unfortunate that the considerable developments which have taken place in the casting and rolling processes, essentially in the direction of high-speed continuous production employing large heavy-unit pieces, have not been matched by corresponding developments in the heat-treatment process. An increasing proportion of the rolled stock delivered from the mill is in the form of very heavy coils which, because of the limitations of existing heat-treatment equipment, have to be cut up into single flat sheets or very small-weight coils before the material can be heat-treated. In consequence, not only is that process slow, but the following finishing processes such as flattening, shearing, and slitting are also slow. Something of the order of half the total cost of producing the saleable product is represented by the cost of heat-treatment and final finishing operations.

Present available methods of solution heat-treatment are, of course, well known. If the final product is to be in flat sheet form, the rolled coiled strip is cut up into single sheets which are supported in racks or suspended from frames, and then either immersed in a salt bath or placed in a high-speed air-circulation furnace.

If the final product is required in the form of coiled strip, the original rolled heavy coil has to be cut up into much smaller pieces and the latter then re-wound with the laps spaced from each other, either by dimpling the edges or interwinding spacing wires. This spacing is essential to ensure that the heating medium penetrates to all the laps (so that the required heat-treatment temperature is rapidly and precisely attained) and that quenching and drying are effective, and in the case of salt-bath heat-treatment to enable any traces of salt remaining after quenching to be washed out. Obviously the width of the space between laps is considerable by comparison with the thickness of the

metal; therefore the over-all diameter of the heat-treated coil is far greater than that of the original coil, and this is one of the factors which limits the weight of the coil that can be heat-treated. Another factor is that in spite of spacing of the laps, the gaps between them cannot be very great; on quenching they tend to close up, and if the quench is to be effective and rapid right through the coil, experience has shown that there is a limit to the width of strip in coil form that can be heat-treated. This is of the order of 36 in. maximum. Further, to provide the minimum spacing that is required, it is necessary in the case of the wider strip to keep the laps apart, not only at the edges but along the centre of the coil, by centre dimpling or threading through a central wire, and in final processing the dimpled zones or the marks left by the wires have to be removed by slitting, thus still further reducing the width of the coil and its finished weight.

Moreover, with existing methods of heat-treatment, thermal inefficiency arises owing to the necessity for repeatedly heating the frames and cradles used for supporting the metal.

Briefly, whereas the casting and rolling processes are efficient by virtue of making use of unit pieces of 2000-lb. weight or more, heat-treatment plant has not been developed on the same scale, and the handling of single sheets varying in weight, say, from 10 to 30 lb., or single coils varying in weight, say, from 50 to 200 lb., makes the heat-treatment and finishing processes much more costly than they need be. An important point that must be borne in mind is that the individual handling of so many small-unit pieces considerably increases the risk of damage to the product, as well as calling for the employment of a disproportionate amount of labour.

Most producers, in view of these circumstances, have contemplated the advantages that would accrue from a continuous method of heat-treatment, whereby a coil of finished width would be drawn successively through a solution heat-treatment zone, quenching and drying zones, flattening rolls, and then either through a flying shear for cutting to dead length, or on to a re-winding drum. In such a development a furnace on somewhat similar lines to that described under Section IX dealing with "Grain-Size" would be required, and the same considerations would apply. In addition, there would be the further complication of providing a rapid quench. The obvious quenching medium is water, but this involves a subsequent drying operation, and it would be preferable if some other method could be developed which avoided subsequent drying or cleaning. The quench should take place as rapidly as possible, preferably within two or three seconds of the strip leaving the heating zone, and this factor would determine the speed of passage of the strip through all sections of the line.

As in the case of the continuous strip furnace envisaged for flash annealing, the continuous strip heat-treatment flattening and cutting-off lines would have to be very carefully designed indeed in regard to the close speed-matching of the component parts and the shape and material of all supporting media, with a view to preventing damage to the metal.

Continuous heat-treatment on the lines described would not only show considerable production economies over present methods, but because the material is held flat and under some degree of tension throughout, the material might suffer less distortion, and if the quench could be made effective and rapid the properties should be more consistent.

XI.—SHEET FINISHING.

With the larger sheets the finishing, i.e. post-rolling, operations of flattening, stretching, and shearing are responsible for a very large proportion of the total cost of production of such sheets from a modern rolling mill. To derive full benefits from these modern mills the production unit or piece should be maintained in its large heavy form for as long as possible throughout the finishing operation.

This principle is followed in the finishing of thin short sheets such as are required for box-making, or for sheets for subsequent corrugating, where the coil is fed through trimmers, roller levellers and flying shears, and cut to length. The reason why the same principle cannot be adopted in the finishing of larger sheets, particularly those calling for a fairly high degree of flatness, is that roller levellers, in addition to tending to mar the surface finish of the sheet, will not give the flatness demanded, and a stretching operation is usually needed. There is, therefore, scope for designing either a continuous stretching machine or a roller-leveller line which will give the desired flatness without, at the same time, introducing surface defects. Such equipment would result in very considerable economies indeed by reducing scrap, eliminating individual sheet handling at several stages, thereby minimizing the risk of damage, and reducing inter-operational transport.

XII.—CONCLUSIONS.

This paper has drawn attention to a large number of production problems still facing the aluminium rolling industry, and in nearly every instance they will require for their solution the closest collaboration between the production engineer, research laboratory staff and, in many cases, plant manufacturers.

The very general adoption of semi-continuous casting has represented a considerable advance in technique, but it seems probable that

there is still much to be gained by further developments in the process. Casting speeds, for instance, are at present limited to a few inches per minute. If these speeds could be materially increased it would not only lead to increased outputs but to many other incidental advantages. The problems here are related to heat-flow and mechanism of solidification which involves co-operation between the metallurgist and the physicist, but any modification to present technique is likely also to involve the plant designer and engineer.

The formation of blister on the surface of aluminium sheet, both pure metal and alloy, has been a constant source of trouble to the industry in the past. Works' trials, in which the different variables have been controlled in an attempt to determine which are mainly responsible, have usually ended in disappointment. The more scientific method of attack, in which an accurate knowledge of the solubility of gases in both solid and liquid aluminium has been combined with accurate methods of gas analysis, has taken us much nearer to the solution of the problem. Further work in this direction by the physicist in close co-operation with the production staff, is still required.

The problems in the field of roll cooling and lubrication require for their solution the joint efforts of the oil chemist, the engineer, and the metallurgist, since the properties which are desirable from the point of view of mill operation are often detrimental from the point of view of metal quality in the finished product.

The control of grain-size and directionality in the finished sheet which is to be used for deep-drawing and pressing operations, is very closely related to the work done in hot and cold rolling combined with appropriate annealing conditions. The most efficient operation of the mill does not always lend itself to the introduction of anneals at the most suitable times. Here again team-work between the scientist and the production staff is essential.

It is, however, probably in the field of heat-treatment and annealing that co-operation between the plant designer, the production staff, and the metallurgist is most urgently required at the present time. The full benefits of modern plant giving high outputs of continuously rolled strip will not be achieved until annealing and heat-treatment facilities to keep in step with output have been developed.

There are several ways in which the problems of the type indicated can be tackled. In the early days of the industry the solution of these production problems was usually attempted by the method of trial and error, in which the various factors which it was thought might influence the result were deliberately varied in the pious hope that all other factors would remain constant. This was a laborious procedure and, even

when a satisfactory process had been found, it was liable to go off the rails, and in the absence of fundamental knowledge it was often difficult to know to which variable the trouble was to be attributed.

The application of statistical analysis to production data seemed to offer some hope, but our experience over many years shows that this method by itself is likely to be disappointing.

An alternative method of attack is to study in the research laboratory the fundamental chemical, physical, or metallurgical facts which are operative in the process under consideration. When this knowledge has been acquired it is usually possible to devise means of measuring and controlling accurately those variables which are important. For example, the ability to control blister in rolled sheet has been enormously advanced by an accurate knowledge of the solubility of hydrogen in solid and liquid aluminium and by having accurate and fairly rapid methods of analysing the amount of gas present in the metal. The study of the various factors which produce directionality in rolled sheet, based on X-ray diffraction and metallographic studies, is making it possible to devise production schedules which will reduce this factor to tolerable limits. Further, it is only by a determination of the constitutional diagram for the more complex alloys that the best heat-treatment schedules and optimum composition can be determined.

These are the sort of contributions that the scientist can make to the development of the industry. His knowledge, however, must be translated into terms of production, and large-scale production at that. This cannot be achieved without the close co-operation of the works production, technical, and engineering staffs, and, in many cases, the plant manufacturers. It is only by such means that progress to date has been made, and this harmony of aims and efforts must still prevail if the industry is to look forward to a successful future.

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SEGREGATION AND LIQUATION OF ALLOYS 1191 AND THEIR APPLICATION TO NON-FERROUS METALLURGY.*

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SYNOPSIS.

After a brief survey of the various stages of solidification, the first part of the paper is devoted to a general survey of the phenomena of segregation in alloys, under the headings of major segregation, minor segregation, and segregation after solidification. Major segregation alone is studied in detail.

Major segregation takes place by diffusion or by relative movement of phases (decantation, inverse segregation). The principal factors governing segregation are reviewed.

The second part of the paper treats of the industrial application of segregation (liquation). This can be divided into liquation on freezing or melting (desilvering of lead, removal of iron from tin, silicon treatment of hard tin, removal of copper and antimony from scrap white metals, production of Alpac, removal of bismuth from lead, preparation of porous metals), and liquation for the separation of two liquid phases (refining of iron-bearing zinc scrap, segregation of iron and tin in the iron-tin system).

In an Appendix there is briefly described the procedure for the refining of work-lead due to M. Léon Jollivet of the Société Minière et Métallurgique de Peñarroya.

I.—INTRODUCTION.

1. *Solidification Stages.*¹

IN the study of segregation, as in that of all other casting phenomena and characteristics such as castability, piping, shrinkage, blowholes, and cracks, the solidification process of metals and alloys can be divided into three stages.‡ These are :

Stage 1 : Crystals of the solid phase are not yet sufficiently developed to touch one another, and swim in the liquid. *The solid phase is dis-*

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§ The process of melting can equally well be divided into stages which are of some interest in the study of brazing and soft solders. From the foundry aspect, consideration of the freezing range and proportions of solid and liquid phases is insufficient, and the solidification stages, which are related to the solid-phase structure, must also be taken into account. The same applies to the investigation of alloy properties at room temperature, where structure as well as composition is important.

continuous and the liquid phase continuous ; the two are capable of relative movement.

Stage 2 : Crystals of the solid phase are sufficiently developed to touch each other or the mould walls and, when immobilized, form a mesh through which liquid can circulate like water in a sponge. *Both solid and liquid phases are continuous, but only the liquid is capable of relative movement.*

Stage 3 : The solid-phase crystals are so far developed as to form barriers restricting movement of the liquid. *The solid phase is continuous and the liquid phase discontinuous ; relative movement of the two phases is impossible.*

It is understood, of course, that on account of temperature gradients during freezing these various stages do not take place simultaneously throughout the casting, but succeed one another; this asynchronism is responsible for major segregation and shrinkage, as well as for the distribution of blowholes and minor or dendritic shrinkage. Accordingly :

(a) Major shrinkage (piping) occurs only after the onset of stage 2, the first stage having only an indirect effect on subsequent shrinkage. Major shrinkage ends with the second stage; after that, only interdendritic- or micro-shrinkage can occur.

(b) Similarly, primary gas cavities (blowholes) do not form until stage 2 begins, and in stage 3 only interdendritic gas cavities or "micro-blowholes" can form.

(c) Cracks do not develop until the beginning of the second and third stages.

2. Crystal Forms and Stages of Solidification.

The factor which governs the stages of freezing or melting is neither the proportion by weight of solid phase, nor its proportion by volume, but what may be termed the *spatial development* (i.e. space taken up), which depends on both the proportion by volume and the external crystal form. The latter can be extremely variable and difficult to characterize geometrically. It may be observed that this obstruction increases with the ratio of surface area : volume, greater obstruction being presented by slender, filiform, and branching structures.

Taking a very simple example, for a cube of side e , the ratio $\frac{\text{surface}}{\text{volume}} = \frac{6e^2}{e^3} = \frac{6}{e}$. Let n be the number of elementary cubes of side e which are assembled to form the cube of side e . If these n elementary cubes are now assembled in rows, every cube having one face common

with its neighbour, the ratio $\frac{\text{surface}}{\text{volume}}$ is then (whether the row is branched or not) :

$$\frac{4n\epsilon^2 + 2\epsilon^2}{n\epsilon^3} = \frac{2(2n + 1)}{n\epsilon}$$

where :

$$\epsilon = \sqrt[3]{\frac{e^3}{n}} = \frac{e}{\sqrt[3]{n}}$$

When n is large this reduces to $\frac{4}{\epsilon}$.

II.—SEGREGATION IN ALLOYS.

1. Definition and Description.

Segregation is a phenomenon which accompanies the solidification of alloys and which causes *differences in chemical composition* between various points or regions of the mass after solidification. Conversely, composition differences through the mass alter the melting temperature (different points on the solidus). On heating a segregated sample, the action of physical forces such as gravity, centrifuging, or compression, will bring about progressive separation in decreasing order of fusibility, or *liquation*. Two words are used for the same phenomenon according to the context :

segregation (detrimental aspect).

liquation (useful aspect).

Littre's dictionary gives :

segregation : action by which one sets apart, separates from the whole, or from a mass. Etymology : from *segrex*—separated ; *se* indicating separation and *grex* a flock or herd.

liquation : separation, one from the other, of heterogenous liquefied substances. Etymology : from *liquare*—render liquid.

According to its extent throughout the sample and the scale of size of the phenomenon two forms (macro- and micro-) are differentiated, as in the study of all other casting phenomena.

(a) *Major Segregation* (also *General* or *Macro-Segregation*). (*La Ségrégation majeure ; Block-Seigerung*.)

This occurs throughout the whole casting and can be detected qualitatively by macro-etching, and quantitatively by *chemical analysis* of areas selected by macroscopic examination (which includes radio-

graphy). It can be completely defined numerically by *isochemical surfaces*, i.e. surfaces of constant composition.*

(b) *Minor or Dendritic Segregation (also Micro-Segregation)*. (*La Ségrégation mineure ou dendritique ; Interkristalline Seigerung*).

This occurs in the core of primary dendrites, is not detectable by normal analysis (macro-analysis), is revealed indirectly by development of the macrostructure (notably Paic's macrostructural radiography for light alloys †) or of the microstructure. Micro-segregation causes the appearance of dendrites in etched metallographic sections. This generally implies a variation in composition of the solid phase with temperature (solid solution), but small inclusions (e.g. in steels) can also produce dendritic segregation.

Micro-segregation is revealed qualitatively by the attack of reagents, and in certain coarse dendritic structures, micro-analysis on micro-samples has been possible. Recourse may also be had to spark spectrography. Convey and Oldfield² used a condensed spark giving a crater of 0.4 mm. by 0.02 mm. deep. In this way the variation in content of carbon, silicon, manganese, nickel, chromium, molybdenum, and vanadium in steels could be determined. In favourable cases the degree of minor segregation can also be estimated from thermomagnetic analysis.

The solidification rate influences minor segregation. Slow cooling allows more diffusion and favours homogenization; on the other hand, it promotes growth of large dendrites and therefore increases the distance between points of different composition. Here we have two opposing effects of which the second often predominates.

(c) *Segregation after Solidification*.

Minor segregation after solidification has also two other forms :

(i) *Minor segregation during transformation*, e.g. separation of ferrite or cementite in "ghosts" and banding, due to precipitation of carbide in austenite containing chromium.³

(ii) *Dynamic segregation* in forgings, due to differences in viscosity of constituents (e.g. formation of gneiss).

Only major segregation will be considered in the following sections.

* See for example the results of Wüst and Felser (*Rev. Mét.*, 1910, 7, 1098) relating to carbon, manganese, sulphur, and phosphorus in steel ingots of various sizes, and the results for carbon, phosphorus, and sulphur in unkilld steel.

† M. Paic, *Rev. Mét.*, 1944, 41, 169; absorption of X-rays being an atomic characteristic, the variation of concentration of a constituent is revealed by a radiograph: the radiographs from a plane-parallel specimen and a step-wedge of some reference metal (e.g. copper for aluminium-copper alloys and zinc for aluminium-zinc alloys) are compared photometrically.

2. Cause of Major Segregation.

Suppose that, by melting and agitation, the liquid in a mould is rendered uniform in temperature and composition. Differences in composition can arise only in two ways: (a) by migration of atoms diffusing through the liquid until stage 3 begins (solid diffusion is relatively too slow to be appreciable); (b) by relative movement of phases.

What determines the operation of these two mechanisms? To take a concrete example, let us consider an alloy of metals (*A*, *B*) in which *B* reduces the melting point of *A* according to the classical behaviour of solid solutions.

(a) Segregation by Diffusion.

Diffusion between two points in a liquid solution may be caused by temperature gradients and composition gradients. Cooling requires a temperature gradient between the inside and the outside of the melt. In a homogenous liquid the Ludwig-Soret effect has been invoked to account for concentration differences, but experiments on alloys (notably by Benedicks and by Ballay) show that the effect is much too feeble to explain the observed deviations of composition in major segregation. On the other hand, in a liquid freezing with a temperature gradient, the temperature differences produce concentration gradients on account of the law of solidification of solid solutions; and before the third stage, while the liquid phase is still continuous, diffusion of element *B* may proceed from regions of high concentration and low temperature to those of lower concentration and higher temperature. In this way the parts freezing later and nearer the middle are enriched in element *B*. This is direct segregation, which may be called "centripetal".

If the crystals are considered as growing in a solid shell from the walls, the front advancing into the liquid may be visualized as accompanied by a concentration wave extending increasingly ahead of it as the temperature falls and the solidification rate is reduced; such segregation is favoured by increase in size of the mass.

The best known and most important example of direct segregation is provided by carbon in steel. It is found also⁴ in copper billets where the top end, which is the last to freeze, is enriched in oxide. This must be attributed to the rejection of reacting gas during solidification.

In a direct casting, the surface is stronger than the interior, which is desirable industrially, for the probability of the occurrence of casting defects is normally greater at the centre than near the surface. If the alloy comprises a mechanical mixture, a slight enrichment of one or

other component is of little practical consequence. For this reason, this type of direct segregation is of relatively small interest, and it is also less common than inverse segregation, of which more will be said.

The necessary conditions are : a freezing range, and a temperature gradient. Besides these two factors the rate of crystallization governs the relative importance of the solidification stages, and the duration of diffusion or freezing depends largely on the size of the casting.

(b) *Segregation by Relative Movement of Phases of Different Composition.*

Consider a mixture of two phases α and β , differing in composition, of which at least one is liquid. Two kinds of displacement are possible :

(1) α is dispersed throughout the liquid β , from which it can be removed by settling or decanting, whether it is liquid or solid.

(2) α is a continuous solid and the liquid β can be removed from it (so-called centrifugal or inverse segregation).

(i) *Segregation by Decantation or Sedimentation.*—This can occur either with *immiscible liquids*, where one is dispersed in droplets in the other, or more generally in the *first stage of solidification* where the solid phase is dispersed in the liquid. In both cases, if there is a *difference in density* resulting from a difference in composition between the two phases, a force field, such as that due to gravity or centrifugal force, will separate them. This applies also to solid or liquid particles present in the melt before freezing, i.e. inclusions of undissolved impurities such as oxides, sulphides, or silicates (which are in fact primary crystals of the metal-impurity system). The suspended particles settle with a limiting velocity given by Stokes' law :

$$V = k \cdot \frac{d_1 - d_2}{\eta} \cdot r^2$$

where d_1 , d_2 are densities of the two phases, r the particle radius (assumed spherical and very small relative to the transverse dimensions of the vessel), η the coefficient of viscosity of the liquid at a given temperature, k a coefficient which is a function of the acceleration due to the force (g for gravity, γ for centrifugal force.) Thus for glass balls in water the times to fall 1 cm. will be :

Diameter, mm.	10°	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵
Duration of fall	0.05 sec.	5 sec.	14 hr.	58 days	16 years	

Industrial centrifuges can produce accelerations of $\gamma = \omega^2 R$ of 1000 g ., while in laboratory ultra-centrifuges more than 50,000 g , is obtainable, compared with which gravitational acceleration is negligible. It should be noted that γ increases with the separation of dense particles,

while g remains constant. Hence the marked radial segregation in centrifugally cast iron and steel pipes and bearing metal.*

Thus the degree of segregation by settling depends on the following factors :

- (1) Difference in density of phases.
- (2) Size and shape of particles. Liquid drops may coalesce under surface-tension forces, which does not happen with solids.
- (3) Viscosity of the liquid phase.
- (4) Strength of force field (γ or g).
- (5) Time of settling, i.e. freezing. This increases with the size of the casting. Settling ends before the second stage of freezing.
- (6) Importance of the first stage of freezing, which depends mainly on the freezing range and the crystal forms.

3. Examples of Segregation by Settling.

(a) Immiscible liquids : Leaded Bronzes.

Two liquid phases of different density may exhibit a *double vertical segregation* which increases in degree with the size of the globules, disparity of densities, and amount of separated phase, i.e. penetration of the point representing composition of an alloy in the miscibility gap. The details of these phenomena are very important in leaded bronzes, which are essentially copper lead alloys used largely for bearings, especially those for aero-engines. Major segregation, as well as marked minor segregation, must be avoided and a fine and uniform distribution obtained of lead globules or dendrites amongst the copper dendrites. Segregation must be stopped by a lattice of copper dendrites in the second stage of solidification. This requires a copper content high enough to give the necessary proportion by volume of dendrites, and so to bring the effective composition of the alloy outside the immiscibility gap.

In the miscibility gap it is impossible to avoid segregation because the liquids separate before dendrites form. Dendrite growth is favoured by rapid cooling, which is an essential factor.

The structure may be modified either by reducing the zone of liquid immiscibility, so reducing major segregation, or by altering the velocity of directional crystallization of copper rich primary dendrites. Numerous additions have been recommended, particularly nickel, chromium, lithium, beryllium, and zirconium, but published evidence

* Liquation of tin has been observed in centrifugally cast nozzles of 8%-tin bronze, but this may have occurred in the second stage of solidification.

is often contradictory; cooling conditions can alter the structure so much that stringent control of experimental conditions is necessary to obtain reproducible results. In fact, despite claims in the literature and patents, no addition appears to have an appreciable effect in promoting fine and well dispersed structures in leaded bronzes. This can only be achieved by a well established freezing procedure.

Cooling must be vigorous, uniform, and well distributed for best results, and casting may be static in a mould, centrifugal, or on steel strips, which are side-trimmed, bent, and machined for bearings.

According to Northcott, all added elements except lead reduce the rate of growth of the copper dendrites.

The layer of bronze cast on the chill steel mould must be as thin and uniform as possible, a variation of $\frac{1}{2}$ mm. being sufficient to alter the structure. Even oxidation of the mould surfaces, by reducing the cooling rate, is unfavourable. To avoid such oxidation, steel (chill) moulds are heated in salt baths or controlled atmospheres.

In any case, the multiple additions advocated in numerous patents for reduction or suppression of segregation in leaded bronzes are apparently ineffective. Only systematic study based on scientific principles and metallography has solved the problem in aircraft bearings.⁵

(b) *Segregation of Primary Crystals in the 1st Stage of Freezing.*

(i) *Hyper-Eutectic Grey Iron* (or ferro-silicon carburized in a cupola).—Graphite is primary and of very low density ($\simeq 2$ as against approximately 7 for the iron). Consequently, being in large plates, it rises at such a velocity (according to Stokes' law) that it not only reaches the surface but projects above it, as was found by Goerens with pieces of wood in mercury. This reduces the carbon content of the iron to the eutectic value.

(ii) *Mild Steels*.—In large mild-steel ingots, cooling slowly, primary crystals, which are low in carbon and therefore more dense, sink to the bottom, where they accumulate in a zone of low carbon content.

(iii) *Anti-Friction Alloys of the Tin-Lead-Antimony-Copper-Type*.—With lead contents exceeding 20%, the compound SbSn segregates upwards in the form of compact polyhedral crystals. This can be counteracted either by rapid cooling in thin sections (as for lead-antimony alloys chill cast into type), or by additions when slow cooling is unavoidable. According to Dannenmuller, 2.5% of copper is sufficient to give needles of CuSn (enclosing Cu_3Sn) which prevent upward segregation of SbSn in lead- and tin-base bearing alloys. Alloys of lower lead and tin content (e.g. less than 5%) require only 1% copper addition to form a mesh of

slender Cu_2Sb needles which prevent segregation of antimony crystals. According to Fournier,⁶ in an alloy of tin 86, lead 3, antimony 8, copper 3%, the presence of aluminium in amounts as small as 1% results in upward segregation of the aluminium as CuAl_2 and AlSb , taking with it a high proportion of copper (10 at the top, 2 at the bottom) and some antimony.

(c) *Segregation of Inclusions Before or During Solidification.*⁷

(i) *Steels.*—Liquid inclusions belong in fact to a bi-liquid system of steel—impurity, or if the inclusions are solid, they belong to the onset of solidification of such a system, and correspond to one of the two previous cases. In particular, sulphide inclusions, having a density of 4–5 tend to rise, forming high-sulphur zones in steel ingots. This is counteracted by the agitation from released gas in “rimming” steel ingots (unkilled steel). Sulphur is removed to some extent in this way as manganese sulphide in the holding furnace.

Consideration of this behaviour indicates the following conditions for refining an alloy :

(1) Impurities must be insoluble in the liquid. For this reason Cu_2O and FeO cannot be removed from liquid copper and steel, respectively, as they are soluble. They must be replaced by insoluble oxides, which are obtained by addition of reducing agents (called deoxidizers) : manganese, silicon, and aluminium for iron and steel; phosphorus, aluminium, silicon, and cobalt for copper. The oxygen merely changes its partner, but produces a precipitate in the liquid in consequence.

(2) The rate of separation of insoluble impurities must not be too low; accordingly, the particles must not be too small. In this respect, solid particles such as SiO_2 and Al_2O_3 in steel, and alloys of copper and aluminium, have the disadvantage of being unable to coalesce like liquid particles. The latter, being droplets which fuse on contact, tend to grow, and the rate of separation increases correspondingly. It is therefore desirable to combine impurities, such as oxygen and sulphur, in a form which is both *insoluble* and *liquid* in the melt at normal casting temperatures. This is achieved with manganese and iron silicates in steel and manganese sulphide in cast iron and steel.

(ii) *Aluminium.*—Aluminium, as drawn off from the electrolytic cell, contains insoluble impurities such as sodium (density 0.9) and inclusions from the electrolyte. It is customary to attempt to remove them by settling in a holding furnace. Raising the temperature, in so far as it reduces the metal viscosity, assists refinement, especially as the density of the inclusions (2.1 — 2.25) differs very little from the density

of aluminium (2.4 at 950° C.), and they are only liquid above 935°–950° C. Both tensile strength and elongation of the aluminium are improved by an increase in the holding-furnace temperature from between 700° and 800° C. to between 900° and 950° C. Higher temperatures similarly favour the removal of alumina from molten aluminium.

Such settling (or flotation) also tends to occur in steel works mixers, in tundishes during the casting of brass, and in feeder heads of castings (incorrectly referred to as filtration). The liquid-metal stream is retarded by enlarging the cross-section of the runner and the pressure is reduced at the ingate.

4. Segregation by Relative Movement of Liquid.

If, during the second stage of solidification, the residual liquid (richer in elements which reduce the melting point) is expelled, the composition of peripheral zones approaches that of the lower-melting constituents. This is in the opposite sense to normal segregation, whence it is described as inverse segregation.⁸ It is very common in the following alloys :

Copper-lead, copper-tin (bronzes), copper-manganese, aluminium-zinc, aluminium-copper (Duralumin) and silver-copper (the major constituent being named first in each case). Various causes have been invoked to account for this behaviour.

Some are hypothetical and unsatisfactory, e.g. different rate of growth of dendrites on the crystallographic axes perpendicular and parallel to the mould walls (Bauer and Arndt⁹); pressure of solidification (Masing and Haase¹⁰).

Capillary action has been visualized as a cause. With large marginal dendrites, capillary forces will draw liquid from the interior along interdendritic channels where the higher-melting constituents will deposit, progressively enriching the liquid in lower-melting constituents as it is drawn towards the mould wall. This phenomenon is said to be accompanied by *interdendritic shrinkage* in the central region of the casting. This is confirmed by tin bronzes, especially if they contain aluminium and iron (deriving from scrap aluminium bronze); in the presence of lead there is even liquation and porosity.

In addition, it has been observed that variations in chemical composition of a casting can arise from micro-shrinkage or interdendritic shrinkage for the core of the dendrites contains less of the lower-melting constituents than the bulk of the alloy. This constitutes apparent inverse segregation, as the micro-shrinkage regions, being

the last to solidify, have a composition corresponding to an alloy of higher melting point. Examples occur in many alloys, especially tin bronzes as shown by Guillet, Galibourg, and Ballay.

It may also be recalled that, in steel ingots, V-shaped segregations on the axis appear to be connected with temporary shrinkage cavities more or less filled with the impure liquid (segregation by displacement of the liquid) and accompanied by a central collapse of the growing crystalline structure (Hultgren).

The pressure imposed by contraction of the solidified shell has been suggested as a cause, but it may be argued that the shell will be at once too rigid to transmit the pressure and too porous to contain the liquid. Kühnel¹¹ maintains that the outer layer solidifies very rapidly, then contracts, thereby exerting pressure on the interior zones (both partially and completely liquid), so that liquid of higher concentration tends to penetrate the outer layers.

Inverse major segregation (*umgekehrte Zonenseigerung*), like normal segregation, is favoured by a steep temperature gradient in the solidification zone; by equalizing the cooling of the surface and interior, major segregation is entirely suppressed.

In bronzes, Bauer and Arndt and Kühnel have observed two tin-rich outer layers, particularly at the extreme surface, and have shown that the tendency to inverse segregation is less the narrower the solidification range. One can also see, in leaded bronzes, inverse segregation displayed by an external sheath of about 1 mm. thickness which is rich in lead and corresponds to the monotectic residual liquid. This would be explained by contraction of the copper-rich outer shell allowing the liquid (enriched in lead) to reach the surface through intercrystalline channels. If the casting is stripped from the mould and quenched in water, the channels are blocked and the segregation suppressed. Apparently gas has nothing to do with this, as the phenomenon persists with vacuum melting and casting. There are, however, examples of a definite effect where release of gas during freezing expels residual liquid to form droplets or even a continuous skin containing lower-melting constituents, especially eutectics.

It must be remembered that the increase in concentration of the residual liquid applies equally to dissolved gas such as hydrogen, and to gas released by reaction in accordance with the mass-action law, e.g. for steel:



Consequently, freezing causes delayed release of gas in the liquid, which, if it occurs in the second stage, promotes expulsion of the liquid from the casting.

(a) *Factors Promoting Inverse Segregation.*

The factors promoting inverse segregation are therefore :

- (1) The freezing range, the relative extents of the solidification stages, and therefore the form of crystallization.
- (2) The temperature gradient.
- (3) The release of gas during freezing, to be determined experimentally.

5. *General Factors in Segregation.*

Reviewing the various examples of major segregation which have been given, the following general casting factors will be found :

- (1) A temperature gradient which increases segregation.
- (2) Speed of cooling which reduces segregation.
- (3) The range and stages of freezing, hence the solidification diagram and the crystal form.

Where there is some choice in the alloy composition it should be towards eutectics, peritectics, or solid solutions of isomorphous metals. In this respect the old coinage alloys, with a composition standardized to one part per thousand, provide a remarkable example of the influence of freezing range. Comparing 10%-copper-gold (gold pieces) with 10%-copper silver (silver 5-franc pieces), when cast identically in 13×42 mm. ingot moulds, the copper-gold alloys with a $10-15^{\circ}$ C. freezing range are chemically homogenous to one half part per thousand, whereas the copper-silver alloys with a freezing range of 100° C. show within the same cross-section differences in composition of never less than three parts per thousand.

It must not be forgotten that it is impossible for segregation to occur in a homogenous system where the components are miscible in the liquid state; this miscibility must be interrupted by two or more phases so as to have separation (*démixtion* ; *Entmischung*).

6. *Other Factors Influencing Segregation.*

Segregation by *diffusion* may be affected by under-cooling. Segregation by *decantation* (flotation) may be complicated and restricted by temperature gradients. The crystal form also plays an important part as it affects the *rate of decantation*. Branched or acicular forms separate less quickly than the compact and convex forms and are immobilized by interlocking in the second stage of solidification. Therefore, other factors being equal, segregation is reduced by strongly columnar crystal growth from the mould walls.

Addition of another element which produces an interlocked acicular growth of primary crystals can reduce considerably the segregation

arising from differences in density of the other constituents. For this reason, arsenic is added to antimony tin-lead anti friction alloys. For example, K. H. Wegner¹² gives the following results:

	As, %	Sb, %	Sn, %	Pb, %
Top	0.13	18.57	13.44	67.86
Bottom	0.09	11.47	8.40	80.04
Mean	0.1	15.0	11	74

which gives a coefficient of segregation * for antimony of:

$$\frac{18.57 - 11.47}{15} \cdot 100 = 47\%$$

whereas with:

	As, %	Sb, %	Sn, %	Pb, %
Top	1.69	15.13	11.00	72.18
Bottom	1.54	15.04	10.78	72.62
Mean	1.6	15	11	72.40

the coefficient of segregation * for antimony is:

$$\frac{0.09}{15} \cdot 100 = 0.6\%.$$

7. Conclusions.

Three principal factors are found to govern segregation decantation:

(1) Freezing range.

(2) Speed of cooling, which governs the time spent in the freezing range.

(3) Crystal form.

Segregation due to movement of solid in the first stage, and liquid in the first and second stages, depends on the crystal form being more or less liable to restrict movement of the solid and liquid phases, respectively. It is evident that for the same proportion of these phases, acicular, dendritic, and thin lamellar forms increasingly immobilize the solid and liquid in that order.

To this end, alloys must be sought with a small freezing range which give, at the onset of freezing, crystal forms with a high surface area: volume ratio, whence there arises the possibility of modifying the crystal form in a favourable sense by small additions or by encouraging the growth of large crystals at an early stage in freezing.

Finally, it is useful to recall that changes in the concentration of the liquid phase during freezing, which is an essential factor in segregation, applies to all the elements present, particularly to those not

* Coefficient of segregation of an element in a specimen is the maximum difference in concentration of that element expressed as a percentage of the mean concentration.

customarily determined by analysis, such as gases, in such a way that when the concentration of dissolved gas (or constituents reacting to form gas) exceeds the solubility of the residual liquid, gas is released and cavities may be formed; hence the connection between blowholes and major segregation, e.g. in steels. On this depends also the practical method of estimating gas contents in castings by observing the extent of the gas-porosity zone in small chill-cast ingots (e.g. discs)—a procedure used especially for aluminium. Similarly, cracks may depend on internal stresses on the one hand or segregation on the other; thus Caillaud¹³ has indicated that in centrifugally cast steel tubes (1% Cr, 0.3% Mo, in which major segregation of carbon is 0.38% in 5 mm.) on account of such segregation the expansion of martensite in internal layers causes internal stresses exceeding 50 kg./mm.² and radial cracks in tubes of 4–5 cm. thickness.

III.—APPLICATION OF SEGREGATION : LIQUATION.

As with all other phenomena, segregation can be either useful or undesirable. So far only the latter aspect, which leads to heterogeneity of an alloy when it is desirable that it should be as homogenous as possible, has been considered. But this phenomenon can be turned to good account :

- (a) In *refining* metals by removal of impurities.
- (b) In separating metals from scrap, i.e. *recovery* of useful metals.

Although by definition “segregation” means the act of separating from the whole or setting apart, the term *liquation* will be applied to this operation, thus preserving the old French meaning which Larousse gives as: “an operation contrived with suitable heating to separate a very fusible metal from a less fusible metal to which it is alloyed”. By contrast, in English, *liquation* appears to be associated with inverse segregation,¹⁴ and the German *Seigern* connotes the application of segregation.¹⁵ More generally, liquation is a process of voluntary separation of an alloy into its useful constituents which could be applied to a mechanical mixture of metals and various products, as in the separation of copper and white metals, and zinc white. In these mechanical mixtures melting of one component separates them, which amounts to extraction by melting.

A range of freezing is necessary for such an operation, i.e. the alloy or mixture must not freeze isothermally. Eutectic alloys and intermediate phases of definite composition are not amenable to this treatment.

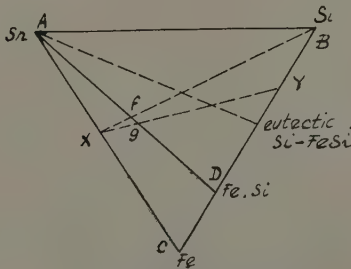
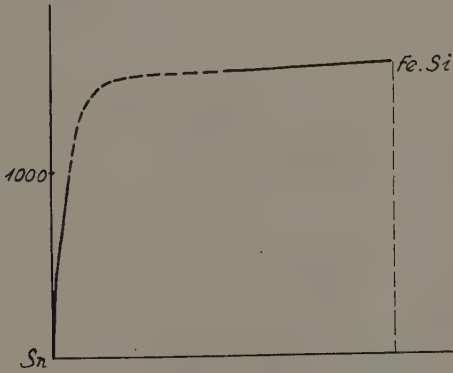
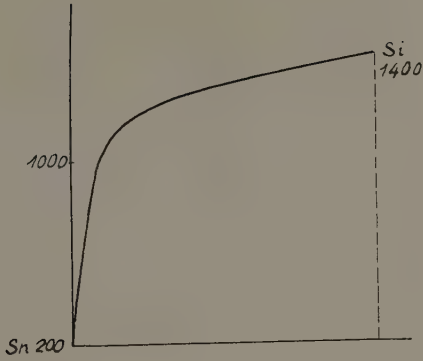
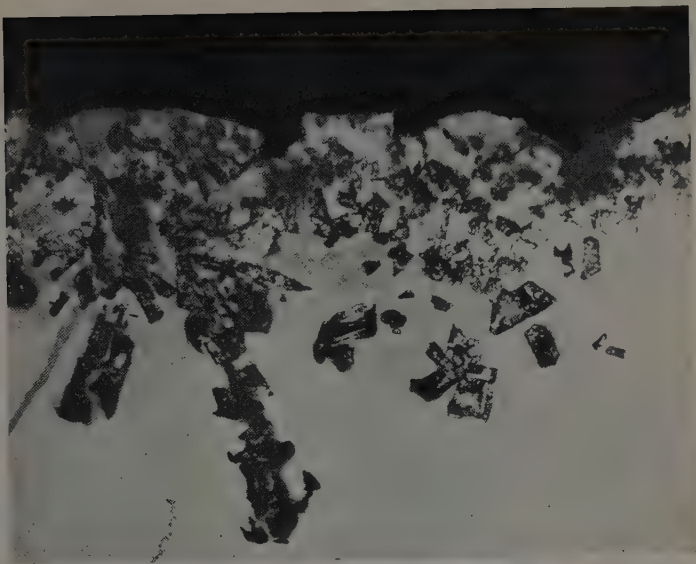


FIG. 3.—Iron-Silicon-Tin System.



FIG. 4.—A Typical Structure in Tin-Lead-Antimony-Copper Bearing Alloy, Showing Possibility of Segregation by Diffusion. Scale is in centimetres.

5



6



FIGS. 5 and 6.—Effect of Crystal Form on Segregation by Decantation of AlSb in Tin-Lead-Antimony-Copper Anti-Friction Alloy. Upper photograph shows small crystals which entrain residual liquid; lower photograph shows well developed crystals which permit efficient separation of antimony.



FIG. 7.—Effect of Adding Zinc to White Metal to Effect Elimination of Antimony.



FIG. 8.—Formation of Silicon Crystals in Production of Alpax by Thermal Process.

As the object is now to encourage instead of to minimize segregation, opposite methods must be used. Principles and operative factors remain the same, however, as the phenomenon is identical, only viewed from another aspect. A freezing range implies partial insolubility of the liquid and solid phases and sometimes of the liquid phases, otherwise known as a miscibility gap, in a system which is partially or totally liquid in the course of freezing or melting.

Liquefaction may therefore be divided into liquefaction on freezing or melting, and liquefaction involving two liquid phases.

1. *Liquefaction on Freezing or Melting.*

As the liquid and solid phases can be separated by settling, centrifuging, filtration, or pressure, it is clear that the three stages of solidification are the primary consideration. Their relative importance depends on :

(a) The thermal equilibrium diagram, which gives their proportions by weight for each temperature and alloy composition.

(b) The relative densities of the two phases, from which proportions by volume are deduced, and which determine whether the solid phase will float or sink during the first stage.

(c) Whether the crystal form is convex and massive, acicular, lamellar, or dendritic and branched ; this determines the obstruction and degree of contact of the crystals.

(d) The rates of crystal growth, which influence the form.

(e) The composition and temperature of the alloy.

It follows that, for alloys which are eutectic at the end of freezing, the primary or pro-eutectic solidification comprises one, two, or three stages, depending on whether the composition is near or far from the eutectic. When an alloy is at a temperature within the freezing range, whether or not the composition is in the region of the eutectic, the primary crystals can be removed from the liquid in the first stage of solidification by settling (decanting), centrifuging, or skimming, a falling temperature and crystals with concave faces being preferable.

For alloys somewhat removed from the eutectic composition, it is better to work in the second stage and to separate the eutectic liquid by drawing off, centrifuging, expression under a press, or by application of gaseous or liquid pressure. A rising temperature and enmeshed crystals (sponge structure) favour this operation. Thus, the methods used may be mechanical or thermal, depending on the various factors enumerated.

The separation is never complete, as the crystals retain some liquid by capillary attraction, the proportion wetting them depending on their surface : volume ratio and the viscosity of the liquid. The operations may be repeated to improve the enrichment, separation, or refinement.

For some refining operations, the impurity is combined with added metals forming components (notably compounds of definite composition) which are insoluble in the liquid and which have physical characteristics, such as density and form, which favour their separation from the liquid, e.g. forming a dross which can be skimmed off the surface. In this process the additions are preferably alkali metals (sodium), alkaline earths (calcium), or zinc and aluminium. Excess additions (generally metals of limited solubility in the alloy to be refined) can be removed subsequently by oxidation.

All these operations require *precisely and easily controlled temperatures*, for which electric furnaces are suitable. When using the cooling process, it should be as slow as possible, hence reduction of the surface area : volume ratio of the melt is advisable by adopting a cubic or a cylindrical shape with equal height and diameter (a sphere being impracticable). A few examples will help towards an understanding of the process.

(a) *Examples of the Application of Liquation in the Course of Melting or Freezing.*

(i) *Desilvering Lead.*—Unrefined lead from most sources contains 0.1–0.5% silver. This is removed either by Pattinson's process (the oldest), or Parkes' process (favoured in the U.S.A.).

In Pattinson's process (or Hall, Luce–Rozan, and other variations of it) the molten lead is allowed to crystallize slowly. The lead–silver system shows a eutectic at 2.5% silver, while the solid solubility of silver in lead is very small. The first lead crystals to appear are therefore nearly pure, and $\frac{2}{3}$ to $\frac{7}{8}$ of the melt can be crystallized in this way; the residual (silver-rich) liquid is separated. The operation is repeated up to ten times in a series of kettles, giving finally a silver-rich liquid (1.5% silver) which, however, does not attain the eutectic composition, and lead containing less than 0.002% silver.

Parkes' process uses a zinc addition to remove the silver as a compound Ag_xZn_y .¹⁶ Fig. 1 reproduces the lead corner of the silver–lead–zinc diagram.¹⁷ The addition of about 2% zinc causes freezing to end along the binary eutectic line *ba*; crystals of Ag_xZn_y rise to the surface forming a crust, which is skimmed off. The final liquid, of composition α , contains practically no silver, but only zinc, which is subsequently removed by oxidation.

(ii) *Removal of Iron from Tin.*—Tin “concentrates” containing iron give, after reduction, an iron-tin alloy containing about 30% iron. As the iron-tin system (Fig. 2) contains a miscibility gap in the

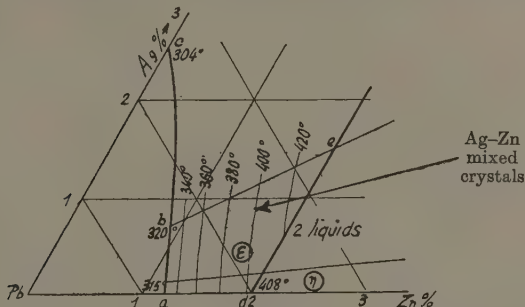


FIG. 1.—Lead Corner of Silver-Lead-Zinc System (R. Kremann¹⁷).

liquid state, the cast metal separates into two layers—the lower one being deficient in iron, while the upper one (hard tin, Hartling) is re-treated. This liquation is assisted by suitable cooling conditions.

(iii) *Silicon Treatment of Hard Tin (Hartling).*—The hard tin obtained in the preceding operation is melted with silicon (or ferro-silicon), which forms FeSi in the course of freezing, and this compound rises to the upper part of the mould leaving a tin-base phase at the bottom. If one adds to an iron-tin alloy of composition X, silicon (B), or ferro-silicon rich in silicon (Y), so as to obtain FeSi, i.e. a composition lying on the line *fg* (Fig. 3, Plate CXX), the minimum of silicon is used, and only FeSi primaries are produced, which favours their segregation. Ferro-silicon should be as rich as possible in silicon to reduce the volume of the separating phase. From Fig. 3 we have :

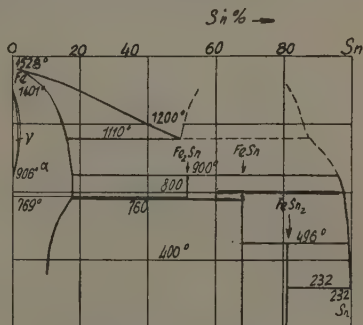


FIG. 2.—Iron-Tin System.

$$\frac{\text{mass of FeSi segregate}}{\text{mass of tin}} = \frac{fA \text{ (or } gA)}{fD \text{ (or } gD)}$$

With careful cooling, the segregated FeSi crystals retain very little tin, and the ferro-silicon is of commercial purity.

(iv) *Refining the Tin*.—After separation of the hard tin (Hartling) as described above, the bottom tin-rich layer is purified by slow crystallization of FeSn_2 , which removes the remainder of the iron. Because the FeSn_2/Sn eutectic is very close to 100% tin, a tin with only 0.05% iron is obtainable; the FeSn_2 crystals, being denser than the melt, fall to the bottom.

The complete process for removing iron from tin is a fairly good example of the various possibilities of liquation: interaction of two liquid phases, long freezing range, relative densities of the phases giving an upward separation (flotation) with FeSi and a downward separation (sedimentation) with FeSn_2 , and a very limited solubility of iron in the liquid eutectic. All this lends itself to multiple combinations. These features are accentuated when the direction of segregation (decantation) is reversed, as in the treatment of lead-tin alloys containing iron.

(v) *Treatment of Tin-Lead-Antimony-Copper Anti-Friction Alloys*.—Crystal form and rate of crystallization play only a secondary part in the examples of liquation so far given, but they predominate in the removal of copper from tin-lead-antimony-copper alloys used to make solders. In these alloys, a remarkable entanglement of large individual crystals with continuous channels between them permits a satisfactory separation from the copper-deficient liquid. A slight temperature gradient even orientates the crystals so that the intercrystalline channels will be open to the surface, making it possible for the liquid to be drained off (Fig. 4, Plate CXXI). This is a typical example of segregation by diffusion.

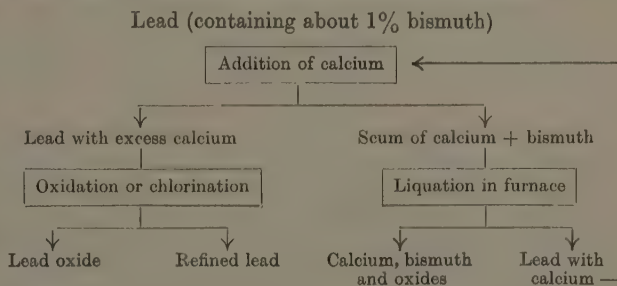
By contrast, removal of antimony from the now copper-free liquid is based on segregation by decantation of AlSb , a definite compound of high melting point formed by the addition of aluminium to the molten alloy. The operating conditions greatly influence the form of the AlSb crystals. This has an important effect, as small crystals (Fig. 5, Plate CXXII) entrain a great deal of residual liquid, but well developed crystals (Fig. 6, Plate CXXII) permit efficient separation of antimony. Here segregation by decantation (flotation) is combined with a marked influence of the crystal form.

Elimination of antimony from white metal can also be effected by adding zinc, which produces the compound ZnSb with convex faces and compact form (Fig. 7, Plate CXXIII), but as this compound will not decant, segregation occurs only by diffusion. Individual crystals growing from the mould walls can attain large dimensions if the cooling

is suitably controlled. However, the crystal form does not lead to a rigid entanglement, and when the remaining liquid is removed, some of the crystals are carried with it causing collapse of the ZnSb skeletal structure. The separation is commercially unattractive.

(vi) *Production of Alpax*.—The eutectic of the 13% silicon-aluminium alloy known as Alpax, can be made by the following thermal process: reduction of bauxite in electric furnace by means of silicon, which results in an alloy containing 30-35% silicon, balance aluminium; on cooling, crystals of silicon separate from the hyper-eutectic alloy. Careful cooling can produce large plates of silicon (Fig. 8, Plate CXXIII), owing to marked diffusion segregation, and the residual liquid (Alpax) is drawn off. The process is analogous to the removal of copper from white metal. The form of the silicon crystals plays a predominant part.

(vii) *Removal of Bismuth from Lead*.—Calcium is added to form with the bismuth a definite compound Bi_2Ca_3 of high melting point (928°C.) which separates as a scum; the underlying lead, now free from bismuth, is then either oxidized or chlorinated to remove calcium. The scum itself is also liquated to recover lead. The sequence of operations can be represented diagrammatically as follows:



This procedure, however, is not very satisfactory because CaPb_3 is formed along with Bi_2Ca_3 and carries away a great deal of lead. The process has been improved in Germany by adding magnesium with the calcium, and in the U.S.A. by adding antimony and magnesium together with the calcium. Betterton and Lebedeff¹⁸ of the American Smelting and Refining Co. describe the operation, which is similar to the desilvering of lead by zinc. The detailed mechanism of the segregation does not appear to have been examined yet, and probably a scientific study of liquation in these alloys would lead to a reduction of the skimmings requiring re-treatment and application of the process to alloys containing more bismuth (e.g. 1%), which are at present refined

electrolytically. An analogous procedure can be used to remove antimony by means of sodium, and copper or nickel by means of zinc; not more than 5% zinc by volume can be added for copper removal, however, as the skimmings would be unduly bulky and retain too much liquid.

The dissociation of binary and ternary compounds in lead-base liquid solutions has been studied by M. Léon Jollivet of the Société Minière et Métallurgique de Peñarroya. It was found that definite compounds of lead with sodium, potassium, calcium, magnesium, zinc, copper, silver, gold, bismuth, antimony, and arsenic dissociate in equilibrium with *free* elements in the liquid,¹⁹ and on this basis a series of procedures for refining work-lead by treatment with zinc, sodium, potassium, and magnesium is detailed in the Appendix* to this paper.

(viii) *Production of Porous Metals*.—By centrifuging, or by the application of gas or liquid under pressure, the liquid phase can be expelled from an alloy in the second stage of freezing, leaving a skeleton or sponge of the solid phase. This process was invented by Professor Hannover, who recommended it for the production of porous lead in accumulators, using alloys such as lead-tin as a starting point.

2. Separation of Two Liquid Phases (*Miscibility Gap in Bi-Liquid System*).

This Section will not deal with the case of separation of two liquid phases lying in the miscibility gap, where they are subject to Stokes' law and have been considered with regard to decantation of insoluble impurities (used for cast iron and aluminium), but rather in relation to the above examples of liquation. After freezing, there is a mechanical mixture of the solid metals and the situation is the same as for metals which are miscible in the liquid state but mutually insoluble when solid. They can therefore be separated by liquation with a rising temperature by heating to just above the melting point of the most fusible metal; removal of copper from lead is an example. Systems of metals which are practically immiscible in the liquid state may be considered here. Two examples are given below.

(a) *Zinc-Lead-Iron System: Refining Iron-Bearing Zinc Scrap*.

Lead is practically immiscible with iron in the liquid state; with zinc, the immiscibility gap extends from 2% to 99.5% zinc but closes fairly rapidly with increasing temperature. By heating to a sufficiently

* Based on private communications from M. Léon Jollivet.

high temperature, galvanizing baths containing accumulated impurities of lead (from zinc) and iron (from attack of molten zinc on dipped articles) become homogenous and then separate into two layers on cooling. The upper layer consists of liquid zinc containing iron and a little lead; the lower layer is mainly lead with some zinc. On freezing, the upper layer grows crystals of iron-zinc compounds which settle to the bottom subdividing the layer into solid zinc (with some lead) at the top, and beneath it, crystals of iron-zinc compounds forming a magma impregnated with residual zinc. Finally, when freezing is complete, the constituents will be separated into three layers:

- (1) Zinc, on top.
- (2) A magma containing iron, in the middle.
- (3) Lead, at the bottom.

Two types of segregation proceed simultaneously in this refining process: immiscibility in the liquid state, and sedimentation of the iron-zinc compounds in the upper layers.

(b) *Iron-Tin System.*

It has been observed above that in commercial processes for segregating iron and tin, the iron-rich alloys separate into two layers.

APPENDIX.

REFINING OF WORK-LEAD.

(Procedure developed by M. Léon Jollivet (Société Minière et Métallurgique de Peñarroya).)

1. *Zinc Treatment to Separate Arsenic, Copper, and Precious Metals.*

Principle.—To the melt of work-lead is added sufficient zinc to cause separation of the arsenic and copper into the pasty surface layer which forms on cooling the bath. The arsenic and copper can thereby be reduced to less than 0.01% without entraining gold or silver. A second treatment with zinc by the normal Parkes' process eliminates gold and silver.

In order that arsenic and copper shall be entirely separated from gold and silver, the quantity of zinc to be added must be carefully calculated. The calculation may be assisted by published thermal

equilibrium diagrams.¹⁹ The zinc required to remove arsenic and copper depends on the concentration of these elements in the lead and the temperature at which the arsenic- and copper-rich layer is separated.

Provided the content of arsenic and copper is not excessive, a single addition may be made of the total zinc required to remove all four elements. Progressive cooling to a temperature ascertained from the diagram will then separate the first pasty layer containing only arsenic and copper. After that, it is sufficient to cool to near the freezing point to separate a second supernatant layer containing the gold and silver.

Practice.—The process hitherto has been carried out in kettles. A first treatment with zinc and separation of the pasty layer near the freezing point eliminates arsenic and copper. Then the lead is transferred to another kettle for treatment by the Parkes' process. This original practice is still important, because large quantities of arsenic can be separated much more rapidly by this means than by oxidation, particularly by the Barris process.

A continuous form of this process is in course of development. Lead will pass successively through a series of deep decanting vessels (similar to the type used at Port Pirie for continuous desilvering, but smaller and differing in some respects). Temperatures throughout the circuit will be stabilized at convenient values, so chosen that the pasty layer formed in the first vessel will contain only arsenic and copper, and that in the second vessel will contain only gold and silver. This process will also be applicable to the removal of antimony and bismuth.

It should be noticed that, contrary to previous practice, antimony is not removed until after the silver; this presents no inconvenience provided that the content does not exceed 0.8%.

2. Zinc and Sodium Treatment to Remove Antimony.

Sodium will remove a substantial portion of the antimony from antimonial lead (by forming binary compounds), but does not permit of the reduction of the antimony to the percentage specified for soft lead. These low antimony contents can be obtained easily by the combined action of zinc and sodium, which form a ternary compound with antimony. This treatment may be applied before desilvering with zinc, because precious metals are not entrained if the additions are properly regulated.

If the lead contains not more than 0.75% antimony, it is more

economical to desilverize with zinc first of all, then to add sodium, which removes antimony by virtue of the residual zinc content (0.55%).

The supernatant layer containing antimony is bulky and easily separated. After sodium treatment, it gives an antimonial lead which may contain up to 40% antimony and zinc oxide. The necessary sodium addition is calculated from the published diagram of the lead-antimony-zinc-sodium system.

3. Magnesium and Potassium Treatment for Removal of Bismuth.

Principle.—Appropriate quantities of magnesium and potassium are added simultaneously to the lead melt, which is then cooled nearly to the freezing point and the supernatant layer removed. The lead should contain as little antimony and arsenic as possible; these would be eliminated along with the bismuth. The lead, so treated, will contain probably less than 0.005% bismuth leaving a dross containing the compound PbBiMgK . The additions are calculated from constants published for the appropriate system.

Practice.—As the dross is readily oxidized, the treatment is preferably conducted in closed vessels. The lead is melted in a kettle from which it is pumped into two circuits. One passes through an electrolytic cell where it picks up potassium, the other is charged with magnesium; the two circuits rejoin in a deep decanting vessel. Here the dross rises into the sealed upper part, from which it is removed at infrequent intervals. The bismuth-free lead runs continuously from the lower part, where the temperature is maintained just above the freezing point.

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MAY LECTURE, 1949.

THE ORGANIZATION AND WORK OF THE DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 1192

THIRTY-NINTH MAY LECTURE TO THE INSTITUTE OF METALS, DELIVERED 25 MAY 1949.

By SIR EDWARD APPLETON,* G.B.E., K.C.B., M.A., D.Sc., F.R.S.

SYNOPSIS.

The foundation and the evolution of the organization of the Department of Scientific and Industrial Research are described. A brief account of the Department's research activities in both peace and war is also given.

I.—INTRODUCTION.

I would first like to say how much I appreciated the honour of the invitation to deliver the Institute's May Lecture. I am, as you will know, not versed in metal science, and was obliged to select as my topic the more general subject of the organization of research. With the approval of your Council I have chosen, within the ambit of that general field, the organization and work of the D.S.I.R., the Government research department in which I have worked during the last ten years. When this decision was taken I was in a position to view the Department from the centre, whereas now I look at it from the immediate outside. But this alteration of position has not changed in any way my firm conviction concerning the important part it can play in our national life, or my warm admiration for the high purpose which animates both its staff and the many advisers who give so freely of their time and thought in furthering its efforts.

II.—THE FOUNDING OF THE D.S.I.R.

Now I think it is always important to remember that the D.S.I.R., a civil research department, was founded during a war—not as a war measure but as a piece of far-sighted planning for the reconstruction period to follow. The Lord President was selected as the responsible

* Principal and Vice-Chancellor of the University of Edinburgh; recently Secretary of the Department of Scientific and Industrial Research.

Minister, and an Advisory Council of eminent scientists and industrialists was appointed to whom all proposals for research were referred for consideration.

The Department's task was to promote and organize scientific research with a view to its application in trade and industry. This was not, however, the first step in this direction which had been taken by the British Government; for, at the turn of the century, the National Physical Laboratory had already been established, and towards its building the Treasury had made a modest capital grant to the Royal Society of £13,000 and a maintenance grant of £4000 a year. When the D.S.I.R. was founded the annual Government grant had increased to £7000, a figure which may be contrasted with the net estimate now before Parliament of nearly half a million.

The problems which the Department had to face in its early years were indeed difficult ones. British industry was then frankly sceptical about the help it could get from science. There were few laboratories, while the number of men of scientific training leaving our Universities was only about a tenth of what it is to-day.

But if we turn over the pages of the early reports of the Department, we cannot fail to recognize the statesmanlike way in which the founders of the Department approached their task and the imagination and vision they exercised in meeting it. In the circumstances the Council might have concentrated the available effort upon one or two isolated problems. They decided, however, to follow the less spectacular, though more statesmanlike, course of devoting their energies to careful planning and consultation, which was to be followed—to quote the words of their first report—"by a gradual and systematic attack upon a wide and carefully selected front". This front, the Council soon saw, must cover three main activities: firstly, the encouragement of fundamental research at the Universities and the training there of research workers to meet the needs of laboratories of all kinds; secondly, the encouragement of research in industry, particularly through the development of the co-operative spirit, both in industry itself and between industry and the Department; and, thirdly, the promotion of research to meet the requirements of Government and the needs of the community.

Although, in fact, the Council addressed themselves first to the organization of industrial research, because they felt the paramount importance of arousing and securing the interest of industry in the application of science, they were, nevertheless, under no misapprehension as to the relation between fundamental science and applied science. They saw in fundamental science—or pure science as it was

then usually termed—the source of new ideas from which the great industrial advances sprang. As J. J. Thomson once said, “Pure science is the seed of applied science, and to neglect pure science is like spending a very large amount on manuring and ploughing the land and then omitting to sow any seed”. The Council realized that their view on fundamental science was neither understood nor appreciated by the industry of that day. In their contacts with industry they were left in no doubt that what manufacturers wanted were quick results, and that most of them were not interested in research which would not produce results within a year. What, therefore, the founders of the D.S.I.R. set out to do was to educate industry to understand what research really was and to appreciate the value of the scientific approach to its everyday problems. The Council believed very firmly that this could best be done by fostering the spirit of co-operation so that the financial risks involved in undertaking research for the first time might be limited and spread over all the firms of an industry. They saw, in the encouragement of co-operative research, not only the quickest means of interesting large sections of industry in research but also of using to the best advantage the limited supply of qualified scientists then available. To quote again from the first report of the Council, “so long as the Englishman treats his business house as his business castle, adding to its original plan here and there as necessity or inclination directs, with his hand against the hand of every other baron in his trade, and no personal interest in the foreign politics of his industry as a whole, it will be impossible for the State to save him whether by research or other means”.

The Council therefore decided to use the lump sum of £1 million, which had been voted to the Department for expenditure on industrial research, in fostering the formation of industrial research associations in various industries, financed equally by contributions from members and by grants from the Department. In embarking on this policy the Council clearly recognized that co-operative effort was no substitute for research by the firms themselves, or, taking the short view, even for research carried out on behalf of industry in existing laboratories. To quote the 1919–20 report, “If the million fund were spent on research at the National Physical Laboratory or in other laboratories up and down the country it might well produce immediate results of much greater value to industry than the same sum spent in subventions to associations that had to buy their experience as well as their staffs and equipment at a time when the country was short of both; but it is only after industries have done research themselves that they can appreciate either its difficulty or its worth . . . had the million been spent on

research directed by the Government itself its effect upon manufacturers would at best have been destructive of their self-reliance and at worst a free gift to their competitors in other lands ”.

But though the Council decided to plan their encouragement of research in industry itself along co-operative lines, it nevertheless recognized that there were many other fields of work which called for independent action by the State. There was, for example, the National Physical Laboratory, for which the Department had become responsible, whose work on units, standards of measurement, and on the determination of physical constants and data of all kinds was fundamental to all industrial activity. There was again the question of the better utilization of fuels, particularly of coal. There was also the question of building, important not only as a capital charge on every industry, but also because of its effect on better housing. Then again, the utilization of imported timber to the best advantage, and the preservation of our foodstuffs through the application of science to the problems of its transport and storage, were also matters for which the responsibility could not be delegated to industry. The Council therefore decided that all these matters could best be dealt with by research organizations, supported by research stations, under the Department's direct control, the results of whose work would be available for all, and whose facilities would provide a central scientific service for Government. Thus in a few years the founders of the D.S.I.R. evolved a plan, or perhaps better a philosophy, for the encouragement and promotion of research in this country which has been broadly followed ever since, with better understanding of detail as the Department gained experience but with few fundamental changes. In their fourth report the Council set out this philosophy as follows :

“ We believe, in the first place, that while it is possible for the State, by means of suitable grants to individuals or the generous support of universities and other independent institutions for research, to encourage the pursuit of research in pure science, it is dangerous and even fatal to attempt to organize it. Research of this nature has no other aim than the creation of new knowledge and is impatient of the control which is inseparable from the idea of external organization. On the other hand, it is necessary for the modern State to organize research, including those simpler types of research which we may call investigation, into problems which directly affect the well-being of large sections of its people. Such researches and investigations deal either with applied science or if they are conducted in the realm of pure science are undertaken with a specific end in view.

“ But in the second place, if the organization of research for public

purposes is to be effective and economical it is necessary to arrange for a central clearing house which will be cognizant of the general lines of research undertaken by different Departments of Government, and a central body connected therewith capable of undertaking or organizing research which it is agreed can best be conducted by one agency in the interests of all.

“In the third place, it is dangerous and even fatal, under peace conditions, for the State to attempt to conduct researches and investigations for the immediate benefit of industries which are not under State management. But this does not preclude the State from encouraging the organization of research within an industry by means of grants-in-aid made under suitable conditions, or even by means of preliminary demonstrations of the valuable results which a well-conducted research may be expected to secure.”

III.—THE INTER-WAR YEARS.

The policy followed by the Department in the inter-war period was in line with the philosophy expressed in this quotation. Assistance was given to individual research workers at Universities for work on projects which were judged to be of timeliness and promise. Grants were made, for example, to Lord Rutherford at Cambridge, which enabled Kapitzka to carry out his work on the production of intense magnetic fields. One of his chief assistants was a young man named Cockcroft, now Sir John Cockcroft, who, as Head of the Atomic Energy Research Establishment at Harwell, holds one of the most important research posts in the country. Sir William Bragg and his group of collaborators at the Royal Institution were similarly supported in their work on the application of X-ray analysis in industry. In an entirely different field of physics my own work on the propagation of radio waves through the upper atmosphere was supported by the Department by way of grants to the Universities of London and Cambridge in which I worked from 1924 to 1939.

I think that the most striking feature which distinguished, and still distinguishes, these D.S.I.R. grants is their complete freedom from unnecessary restrictions and irksome conditions; in fact, practically the only condition attached to them is that any results of importance which emerge from the work should be published. Throughout its existence the policy of the Department has been to select the worker—whose qualities, by the way, are usually displayed in his research proposals—and, having done so, to leave him to get on with his work without further interference.

In the inter-war years the Department also steadily developed its

scheme of maintenance allowances to post-graduate students at the Universities, which enabled them to be trained in research methods by working two or three years under the guidance of a supervisor. The aim of the training provided by the scheme was, not so much to turn out specialists in some narrow branch of science, as to provide the students with an understanding of the research approach to a problem, and to give them that degree of self-confidence which every research worker must acquire.

And here, perhaps, it would not be superfluous to mention something which does not seem to be fully appreciated. Many people seem to have concluded that our research trainees must necessarily work in a University and that the training must be in so-called pure science. I would like to emphasize that this is not the case and that grants may be given by the Department for training in applied science, in the methods of industrial research, and even for courses in technology. The awards may also be held, not only at Universities, but also at Technical Colleges, D.S.I.R. Establishments, Research Associations and, in fact, at any research laboratory or institution approved by the Advisory Council, including, in special cases, industrial works laboratories.

In this connection, I would venture to express a personal opinion. I believe that, in this country, there is a definite shortage of that group of scientific workers whom I will call *research engineers*. Members of this specialized class, are, of course, provided by our engineering schools. But I would like also to see men who have taken high degrees in University Honours Science courses—in physics, in chemistry, or in mathematics—turning to the applied side, by way of post-graduate courses in engineering. It seems to me that men with such a broad fundamental training, if attracted by the challenge of applied problems, may well become, by way of this alternative route, valuable recruits to our Government and industrial research organizations.

But to return to history. In the inter-war years the Department extended the research organizations under its own control, and this branch of its activities soon became the largest. It assumed control of the Geological Survey, and established the Chemical Research Laboratory, while to the organizations dealing with fuel, building, timber, and food, which I have already mentioned, stations were added for research on roads, for the study of the problems of water purification, and, at a much later date, a laboratory for dealing with insect attack on stored products. It is quite impossible to survey even briefly the results which have come from the work of these stations, but I think you would like me to recall a few examples.

Our Food Investigation organization devised and developed on a

large scale a new method of storing apples and pears, known as refrigerated-gas storage, which depends on maintaining a correct percentage of carbon dioxide and oxygen in the atmosphere of the stores. We also developed a method by which beef—which we know to our cost does not take kindly to freezing—could be stored and carried in a chilled condition for a period of 10–12 weeks, long enough to permit it to be brought from Australia or New Zealand. In this process the deterioration of the meat is prevented by the introduction of 10% of carbon dioxide into the holds, which delays attack by bacteria and other micro-organisms. This work was also taken up by the trade, and before the war ships were being built for the transport of chilled beef from the distant countries of the Commonwealth. I have no doubt that when, as seems likely, meat production is further developed in Australia in the future, this discovery will be of importance in ensuring that carcasses reach us in prime condition. Great progress was also made in the storage of fish, and it was found that, by processes of rapid freezing, fish could be kept in perfect condition for many months.

In an altogether different field perhaps one of the most remarkable results of the Department's work, which came from the Chemical Research Laboratory, was the discovery of what are known as ion-exchange resins by Holmes and Adams in 1934. One class of these substances are synthetic resins which are really insoluble organic acids. If, for example, a weak solution of common salt is passed through a tube containing granules of one of these resins, the sodium ions in the salt are exchanged with the acid group in the resin so that what comes out of the tube is a weak acid. Holmes and Adams also prepared other synthetic materials which contained basic groups so that acids, when passed through them, came out as water. Thus, if ordinary tap water is passed through two tubes in series containing the two varieties of resins, what ultimately emerges is a liquid comparable in purity with distilled water. Sea water, for example, treated in this way becomes drinkable.

The Department took out patents for this discovery, which have proved of considerable value to the nation.

Hitherto the chief application has been to water softening for domestic and industrial purposes, but the invention has been applied to the recovery of metals such as copper and nickel from solutions and the purification of sugar and in the treatment of many trade effluents. It is also of use in the preparation of rare metals and the products of uranium fission.

Passing to another field I need hardly remind you of the important metallurgical work carried out by the Department before the war, because many of its results were published in papers to your Institute.

You will remember those on the age-hardening of aluminium and on the preparation and properties of numerous magnesium alloys, and on the methods, such as coating with selenium, of preventing their corrosion. Much of this work, of course, had important applications in the war. There was, again, work on the behaviour of metals at high temperatures which found its application in the design of electrical generating equipment.

But it is impossible to get a true picture of what the D.S.I.R. achieved in the inter-war years by quoting isolated examples of its work. I think few of us, even in the Department itself, realized quite how much progress, for example, had been made by the Building Research Station, until the requirements of the post-war housing programme made it necessary for us, working in collaboration with the Ministry of Works and the Ministry of Health, to make a survey of what was known about efficient building. The first-fruits of this appeared in the series publications known as Post-War Building Studies, and in particular in the report of the Inter-Departmental Committee on House Construction. This report, for the first time, provided scientific and quantitative standards—or, in other words, a yardstick—based on 20 years' research at the Building Research Station, against which the quality of any proposed form of house construction whether traditional or novel, or of any design for a pre-fabricated house, could be judged on a scientific basis.

Again, our Fuel Research Station carried out many important investigations on the carbonization of coal which improved the yield of gas from all sorts of retorts. It worked also on the production of fuel oils from coal, and on the preparation of coal for the market, and in the course of the work collected an immense amount of knowledge. But perhaps the most outstanding achievement in this field during the period was the formation of the Physical and Chemical Survey of our National Coal Resources, which was organized in nine laboratories in the different coal fields with headquarters at the Fuel Research Station. The Survey developed standard methods for the analysis of various coal seams, by means of which the quality and suitability of the seams for various purposes could be assessed. It also collected data from which it was possible to work out with considerable accuracy the properties of the coal at places where it was not yet accessible, so that future mining development could be planned with confidence. The Department always felt that the work of the Coal Survey, dealing, as it did, mainly with the winning and marketing of coal, ought to be carried out by the industry itself. It was therefore natural, when the National Coal Board was established, that the Survey should be handed over to the Board as a going concern, leaving the Fuel Research Station free to develop more

fundamental research and to pay more attention still to problems of utilization.

But returning to the question of organization, it is worthy of note that the encouragement of the co-operative principle, which led our founders to establish the co-operative research associations, was also applied to other activities of the Department, particularly through the setting up of temporary organizations for the study of specific problems. I might mention three of these. Firstly, the study, in which the British Steelwork Association co-operated, on steel-frame building construction, which resulted in a new code of practice being evolved by which about 20% of the steel used in building could be saved. Then again there was the Bridge Stress Committee which, in collaboration with the Railway Companies, carried out a long investigation of the principles involved in the construction of railway bridges. This work is worth recalling because it illustrates how difficult it is to predict the outcome of research, which in this case ended not so much in changes in the design of the bridges as in the design of locomotives. There was, again, the committee which examined the locomotives themselves and the testing of their performance. This committee prepared plans for a full-scale locomotive testing station, but it was not until last year that their proposals matured with the opening by the British Railway Executive of the Locomotive Testing Station at Rugby. This is one of the very few cases in the Department's history where financial considerations have prevented the rapid realization of a really well-thought-out scheme.

Of course, during the inter-war years the Department like everyone else was exposed to the financial blitzes which struck the country. There is no doubt that it weathered the economic storms and the various economy campaigns extremely well. This indicates the high regard in which the Department's work was held. The education of industry in the pre-war years was, however, proving a slow process—slower indeed than the founders of the Department had expected it to be. This is shown in the comparatively slow growth of the co-operative research association movement. The research associations had a very hard struggle to establish themselves, and it is to the credit of everyone that they succeeded as well as they did. Let me quote a few figures. In 1921 there were 21 research associations having a total annual income of about £190,000; in 1929 there were 20 with a total income of about £225,000, and in 1938 there were 21 with an income of about £470,000. Let us compare these figures with those of the present year. The associations now number 40 (incidentally the figure estimated in the first annual report of the Advisory Council as the number of associations

needed to cover the whole of British industry) with an income of about £2 million a year. After making every allowance for the general rise in costs, these figures show a very considerable growth, and there seems every indication that the rise will continue. Provided difficulties in the provision of buildings and the recruitment of staff are overcome I should not be surprised to find that the expenditure on co-operative research approached in the future a figure of £5 millions a year, or even more. Not only has the number of research associations thus doubled since the war, but their scale of working is far higher. Thus, judgments on the research association movement based on pre-war impressions alone are, in my opinion, very misleading. In spite, however, of the altogether inadequate scale upon which most of the research associations had to function before the war, the research association movement became an established and valuable feature of British industry's research effort. All of them managed to do very valuable work for their industries and were, moreover, to make, as we shall see, contributions to the war effort out of all proportion to their financial resources.

This mention of the last war brings me to the ten years during which I was a member of the D.S.I.R. They were strenuous years, for they not only involved preparing the Department for war and ensuring that it gave its all to the country's effort, but they also covered the immediate post-war period with its new problems and new demands.

IV.—THE D.S.I.R. IN WAR-TIME.

In the extracts of the second volume of Mr. Churchill's book which have appeared recently in the Press, you will remember that, when he visited France at the time when resistance was beginning to crack, he asked this question: "Where are the reserves?", and was horrified to hear that there were none.

Looking back it seems to me that the first task the D.S.I.R. undertook in the preparation for war was the creation of a scientific reserve, although I do not think we quite looked at it in that way at the time. I suppose everyone expected that the scientific contribution to the war would be very great and the call for scientists very large; but many of us felt, and as time went on we were proved to be right, that it would be impossible to judge correctly in advance in what direction the final demands would be made. Obviously the demand of the Services for manpower for research on new weapons and on such things as radar had to be met from the first. It was largely met by the arrangements made by the Directors of Research of the Supply Departments for University scientists to leave their laboratories and join the national research establishments. But in this mobilization the importance of research

teams was very present in the minds of all of us, and the safeguarding of their usefulness was entrusted to the D.S.I.R. It was arranged that such teams should not be recruited through the Central Scientific Register of the Ministry of Labour without prior consultation with us. The general policy followed was to leave research teams in industry substantially intact. In the case of University workers, who were generally accustomed to working alone or in small groups, no such attempt was made. I think the decision proved a wise one; the research establishments were strengthened by the assistance of many brilliant minds from the Universities, while the research teams in industry, in our own establishments, and in the research associations retained their striking-power as composite units.

Thus D.S.I.R. remained a separate entity throughout the war and was not dispersed among the Service Departments, although, of course, many members of our staff were seconded to them as required. Gradually the whole Department was drawn into the war effort. At the National Physical Laboratory the Radio Division developed aids to meteorological observation; the Electricity Division was concerned with the protection of ships against magnetic mines. The problems of towing parts of the Mulberry harbour were studied in the Ship Division, where, in fact, models of the vessels which were to be sunk to form the breakwaters of the harbour were sunk in its tanks in the presence of the officers who were to be responsible for the actual operation. Other Divisions worked on the disposal of unexploded bombs, ballistics, the comfort of troops in armoured vehicles under tropical conditions, and on the testing of gauges and instruments required for armament production. Foams for fighting oil fires were developed at the Chemical Research Laboratory, and the resources of our Food Organization were fully mobilized for dealing with war-time problems, particularly with the development of dehydration. Adhesives which made the construction of the "Mosquito" possible were developed at the Forest Products Research Laboratory, and the Fuel Research Station dealt with such matters as the prevention of the emission of smoke by ships in convoy and the production of fuels for flame-throwers. The Geological Survey provided invaluable information for siting camps and airfields, including, in particular, data on water supplies. We were also concerned with the exploitation of D.D.T. and devised a new method of flax retting in which no waste water was discharged into the rivers. Air-raid shelters were largely designed by the Building Research Station from knowledge gained in its study of building materials. Finally, the Road Research Laboratory not only developed methods for laying emergency airfields rapidly and for dealing with mud, but it also

applied its knowledge of concrete to the study of defences and their destruction. Indeed the Laboratory became, in course of time, the acknowledged authority on the physics of explosions and on the design of bombs for special purposes. This work was carried out largely by experiments on models, and the details of the attack on the Möhne Dam were worked out there before the actual operation.

Much of the work undertaken for war-time purposes has, of course, peace-time applications and has been further developed since the war. An instance of this is what is called "ionospheric forecasting", by which it is possible to forecast for some time ahead the wave-lengths which should be employed for long-range short-wave radio communications to all parts of the world. These forecasts are based on observations of the electrical conditions of the upper atmosphere collected from many stations.

Undoubtedly the most important branch of work for which the Department was responsible during the war was the British effort in the development of the atomic bomb, carried out under Sir Wallace Akers, the Director of Tube Alloys Research, the term under which this project was camouflaged. This, however, is not the place to retell that long and exciting story.

The research associations also made, as I have already said, a most valuable contribution to the war effort. The Cotton Research Association produced cotton material in which the fibres are twisted in such a way that they swell immediately when the material comes in contact with moisture and so block the interstices of the cloth which then becomes waterproof without further treatment. Fabrics made in this way, while they are impermeable to water, allow air to pass through them easily. These "Ventile" cloths, as they are called, were used in the war for making waterproof clothing for airmen. The material was also successfully used for hose-pipes. Since the war the principle has been employed in the development of a number of attractive fabrics, mainly for export. The Wool Research Association, on their part, devised satisfactory processes for preventing felting and shrinking of woollen goods, which were widely used in the manufacture of clothing for the troops. The Laundry Research Association advised on field laundries and the best method of washing clothes with little or no soap. It also devised a method of treating blankets with oil which prevented cross-infection in hospitals. These examples can be paralleled from the work of the other associations.

So much, then, for the war effort itself. I now pass on to the post-war years and the future. Our Advisory Council began its planning before the war ended. We all appreciated, I think, that the relationship

between industry and science had changed very materially as a result of the war. Both management and the technical branches of industry had been thrown into much closer touch with academic and applied science and with scientists of all kinds than had ever happened before. Much of the old suspicions and antagonisms had disappeared entirely and the words collaboration and co-operation were taking on new meanings. In the pre-war years, for instance, the Federation of British Industries as an organization had perhaps stood rather aloof from research, but it now set up an Industrial Research Committee, whose formation was a recognition of the fact that the proper use of science and scientific manpower in industry was regarded as a managerial problem of the first order. I feel that the F.B.I. Industrial Research Committee is indeed to be most warmly congratulated on the services it has rendered to the promotion of industrial science in the post-war world, both through the stimulating conferences it has arranged in various parts of the country and through the valuable surveys it has initiated. I need hardly say that relations between the Research Committee and the D.S.I.R. have always been most happy, and that we have welcomed most cordially the opportunities of close collaboration with the Federation which its existence has made so easy and so agreeable.

V.—THE POST-WAR PERIOD.

Our Advisory Council, before the war ended, made a general survey of the development necessary to meet the post-war situation, and each of our Research Boards examined the requirements in its own field. Broadly the conclusion of these surveys was that, while no very material change in the organization of the Department was necessary, the times demanded a very considerable expansion of its work. Plans to this end were drawn up and are being implemented as quickly as possible. Already a good deal has been achieved. Applying the yardstick of finance, the net expenditure of the Department before the war was just under £700,000. The estimates now before Parliament make provision for a sum of nearly £4½ million, which incidentally is an increase of just over a million pounds on the previous year.

Little fundamental research was done in the war, so it became very necessary to take steps to replenish our scientific capital. The main support for the Universities comes, as you know, not from the D.S.I.R. but from the University Grants Committee, but D.S.I.R. is not precluded from supporting special items of research of timeliness and promise. In this year's estimates provision for grants to individual workers and for the allied service of training of young research workers is nearly £750,000 as against £26,000 in the year before the war. A very

large part of this sum goes to financing the construction of various types of particle-accelerators for experiments in nuclear physics; indeed, it is expected in the long-run that this programme of work, which is being carried out in the Universities of Oxford, Cambridge, Birmingham, Glasgow, and Edinburgh, will cost at least £1 million in capital expenditure alone. Such a concentration of effort on one branch of physics has naturally made many people question its wisdom, but I do not agree that the preoccupation of some of our leading physicists with work in this field gives it too strong an emphasis. There are at present no more important scientific problems than the identification of the elementary particles and the investigation of intra-nuclear forces. But I do, however, see a danger of a different character. This large-scale work has to be carried out by teams of workers, and in its conduct many hands and many types of knowledge are required to work out a plan conceived by one brain. I therefore have some doubt whether each member of such a team is likely to get the research training which was possible in much of the physical research of yesterday, in which each individual built his own apparatus and used it practically single-handed.

So much then for our support of University research. Let me now pass on to mention some of the additions to our own research organizations. I will begin as before by comparing the present estimate and the pre-war figure of expenditure, which are £2,700,000 and £840,000, respectively. Here again we have a very large increase. I cannot, of course, hope to deal in detail with the plans of each of our organizations, but, at the National Physical Laboratory, for example, we set up in 1945 a new Mathematics Division, which includes among its sections a General Computing Section which is prepared to carry out for industry and Government mathematical computations on standard commercial calculating machines. There is also a Punched-Card Section and a Differential-Analyser Section, while another is engaged on the construction of an automatic computing engine. The Division also carries out research in statistical theory. Another new section at the N.P.L. is concerned with the applications of electronic techniques, and is ready to advise on their application to the control of industrial processes. On the other hand, we have converted the Radio Division of the N.P.L., which carries out a programme of fundamental radio research drawn up by our Radio Research Board, into a separate Directorate. In time a new station will be built for its work.

Then, we have also set up a new organization for generic research in mechanical engineering. This is to have a laboratory of its own for which we have selected a site in the new town at East Kilbride near Glasgow. In the end this station will probably become one of the largest

in the Department. Another new organization deals with what is known as Loose-Boundary Hydraulics, that is to say, with the study—by means of models—of the changes taking place in rivers, waterways, and estuaries, and the design of harbours, docks, &c. This will also require a new station before it can get fully into its stride. But in the meantime it is making what use it can of the somewhat meagre facilities at present available for extra-mural work. Another new organization set up since the war has been formed jointly with the Insurance Offices to deal with research into the prevention and fighting of fires, safety of life, and mitigation of damage. A number of our existing stations will also require new laboratories, and we look forward to seeing some of them being grouped together in the new town of Stevenage.

Broadly, the programmes of our stations have been considerably re-orientated to meet post-war needs. Research on road safety, for example, has been added to the responsibilities of the Road Research Laboratory. Both our Fuel and Building Research Stations are devoting a good deal of effort to the study of domestic heating. At the Fuel Research Station a new laboratory, known as the Calorimeter Building, has been erected which contains a number of specially designed cabinets, each about the size of a small living room, in which the performance of heating appliances of all kinds can be quantitatively examined. At the Building Research Station one group of eight experimental houses has been built to provide data on the effect of the amount of heating insulation used in their construction on their fuel requirements; while another group of twenty houses is permitting comparative tests to be made on different systems of heating, cooking, and hot-water supply.

As I have said, we have made no very material changes in the organization of the Department itself. I should, however, perhaps mention one, which is the building up of the Intelligence and Information Division in our headquarters.

This Division supplements the work of the Information Sections of D.S.I.R. stations and of the research associations. It has been estimated that these organizations are now dealing *in toto* with at least 100,000 technical enquiries from industry a year. The Intelligence Division also has the task of keeping under survey the research facilities of the country in D.S.I.R.'s field, calling attention to gaps and ensuring that opportunities for development arising from the work of various laboratories are not overlooked.

What did surprise all of us after the war, however, was the way in which the co-operative research associations forged ahead. Rather remarkably, I think, this growth has not been looked upon altogether

favourably in some quarters—not, I may say, industrial quarters—and the suggestion has been made that the money spent on the associations would produce better results if it had been spent by firms in their own laboratories. It is difficult to believe that such an argument could be put forward seriously. To meet it, it is only necessary to quote a few figures. A subscription of perhaps £250 a year in the case of a big firm, or of £25 or even less in the case of a small firm, entitles them to participate in research costing many thousands a year. How much research could be obtained for the same expenditure in a firm's own laboratories, bearing in mind that the survey carried out by the Federation of British Industries revealed that the cost of employing one qualified scientist in a properly equipped scientific research laboratory works out at about £2500 a year. Don't believe, however, for one moment, that we in the D.S.I.R. think that the existence of co-operative research associations renders it unnecessary for any firm to develop its own research organization to the greatest extent it can afford. The two types of effort are entirely complementary, but the fact is that a firm which has a research department of its own is likely to be a stronger supporter of a research association than a firm which has not; and, moreover, it is the better able to get value for its subscription because it can the more readily use and develop the results of co-operative research for its own benefit. The real strength of the co-operative research movement lies in the fact that the things which a self-governing research association does are those which the industry itself, as represented by the association's Council, believes can be better done co-operatively than individually.

As a rule, a newly formed research association is required by its members to undertake work which will give results of immediate value to industry. It begins, therefore, by instituting library and information services, and by tackling the day-to-day problems of its members. Later it embarks on background and long-range research as the only sure foundation for future progress. Such work may in due course lead to the development of new materials, processes, or machinery up to a stage at which the member-firms can take over the results. Comparative surveys and operational research usually figure last in the evolution of research-association activities, since they make the highest demands on technical knowledge and industrial experience.

At present, as I have said, the research associations number about 40, more than half of which have been formed since the war and have therefore hardly had time to get into their stride. This means that the co-operative needs of most of the larger industries of the country are now met, but there are still many problems to be faced. There is, for

example, the problem of the smaller industries. Experience has shown that an association whose income does not exceed £20,000 a year cannot now undertake more than a few of the activities proper to a research association. Sometimes the smaller industries can be advised to seek membership in one of the larger research associations. In other cases industries which are related to one another industrially or scientifically can form a research association to serve their group, but such a course does not always appeal to small industries who wish to maintain their identity. In studying possible post-war developments our Advisory Council spent some time in considering whether an institution on the lines of the Mellon Institute in America should be set up in this country. While the Department has an open mind on the matter, up to the present it has not obtained any real evidence of a demand for confidential sponsored research. This again is an indication, I think, of the degree to which the co-operative spirit has seized the country. There seems to be a stronger case for sponsored development, but again the evidence is not very convincing.

These, then, are some of the problems to which the Department is now giving attention. But the real test of a live organization is the degree to which it can adapt itself to meet the demands laid on it by the changing needs of the time. To-day some of the greatest problems before the country are the need for increased exports, greater industrial efficiency, and increased productivity. Let me end then by examining what sort of a contribution D.S.I.R. and the organizations linked with it can make to the solution of one of these national problems.

VI.—SCIENCE AND PRODUCTIVITY.

If you ask most firms to-day what is the chief obstacle to their using the scientific approach in increasing productivity, most of them will tell you it is shortage of qualified staff. The removal of this shortage depends on the output of trained men from the Universities and Technical Colleges. Thus, although the contribution from the Universities is essential, it is of a long-term nature.

If we turn to our own stations we take a step nearer the consideration of our immediate problem. With the exception, however, of some branches of the National Physical Laboratory and of the Chemical Research Laboratory, most of their work is not directed so much to improving quality or quantity of the products of manufacturing industries as to ensuring what may be called wise national capital expenditure, by providing knowledge by which programmes of public works can be executed efficiently at reduced cost of manpower and material. Their work also leads to higher general standards of life and

working conditions, but here again is directed to increasing over-all national productivity rather than the productivity of individual industries or factories. In these days D.S.I.R. scientists do not sit in their laboratories; they go out into the world to spread their knowledge. For example, half the scientific staff of our Water Pollution Research Laboratory are generally away helping industry with short-term problems, for many new factories would never have been built without, first, the Geological Survey finding the water which they require of the right kind and in the right quantity, and then our Water Pollution Laboratory showing how that water, when it has been used in the factory, can be disposed of without poisoning or polluting the countryside.

The work of our Road Research Laboratory, again, on the surface dressing of roads has shown how their life can be extended from two or three years to five or even twelve years, which means a reduction in the cost of the upkeep of the roads of millions a year. That, I think we would all agree, is a real contribution to over-all national productivity.

I mentioned a little while ago the work of the Building Research Station on domestic heating in the experimental houses. This work has shown that in some cases the fuel requirements of a house can be reduced by nearly 40% a year at the expense of only a small increase in its capital cost. When we remember that nearly 60 million tons of coal are used a year for domestic heating in various forms I need hardly stress the importance of such work as this. The Fuel Research Station has made a direct contribution towards the solving of a problem arising in the operation of electrical generating plant. Many power stations have had to shut down their boilers periodically and, in extreme cases, once every two or three hundred hours, because of deposits on the heating surfaces. As a result of investigations, the Fuel Research Station has shown how boilers can be run for greatly extended periods. During the work our people crawled through the insides of at least 40 power-station boilers, and from what they observed, together with the results of some fundamental work, they were able not only to identify the cause of the deposits but also to show ways by which they might be prevented.

But it is to the research associations that we must look for the greatest contribution towards immediate increased productivity. Perhaps the best known example of such work is that carried out by the Cotton Research Association, which is now being applied by the Cotton Board, in which a comparison was made in the output per operator in different mills making the same kind of products. This work showed that, for the same kind of process and the same kind of yarn, the number of man-hours required for the production of a pound of yarn processed varied from mill to mill by as much as 3 to 1. Moreover, by a study

of the good and bad mills the reason for the difference became clear—labour deployment, packaging sizes, lay-out, and so on. It was also shown that if the practice of all the mills could be brought up to the best, an increase in productivity of at least 10% and in some cases as high as 40% could be obtained with the present labour force and machinery.

The Boot and Shoe Research Association, as well as others, has carried out similar kinds of operational research; for example, by the application of statistical methods to the process of the fitting of shoes, a new system of last-sizes has been evolved which is proving a great success. Thus a system of precision fitting—equivalent to the 120 fittings of the American system—has been evolved with only 30 fittings, so that the number of sizes a shop must keep to satisfy its customers is reduced.

The Boot and Shoe Research Association has also studied the application of infra-red heating in shoe manufacture and has shown that the time required for drying adhesives between the sole and the upper can be reduced from 30 or 40 min to about 2 min., and in another process from between 70 to 120 min. to 1 min. Commercial infra-red dryers are now being produced and some are already in use in the factories.

The research associations serving the metal industries have also made many important contributions. The Non-Ferrous Metals Research Association, for example, has carried out an industrial survey to find the most practical means of applying its recent recommendations for the production of more satisfactory tin bronze, and gun-metal castings. Then the record output achieved by the cast iron industry of $3\frac{1}{2}$ million tons a year, compared with $2\frac{1}{2}$ million tons pre-war, can also be largely attributed to the work of its research association on the improvement of manufacturing processes. To the long list of heat-resisting and corrosion-resisting cast irons which have come out of its laboratories must also be added the remarkable cast iron of great shear strength known as nodular cast iron. This is earning dollars from the U.S.A. under licensing arrangements.

Finally, I should like to quote a further example of work in progress which illustrates a typical piece of co-operative effort between Government, two research associations, and a number of individual firms. This work in the end may well result in an extra million tons of steel being produced a year from our existing open hearth plant. Government factories extracting magnesia from sea water have succeeded in producing magnesite, from which basic refractory bricks, in every way as good as those made from imported materials, can be manufactured. Under the stimulus of the British Iron and Steel Research Association and the British Ceramics Research Association, several open-hearth

furnaces of "all-basic" construction have been built in steel works and are at present giving an increase of 10% of output per square foot of hearth. The new bricks, though more expensive than those previously used, permit furnaces to be driven at higher temperatures which, strange as it may appear, gives them a longer life and so makes the use of the new bricks economic. The research associations concerned are observing and reporting on the trials for the benefit of industry as a whole.

These, then, are a few examples of the kind of contributions the research associations are making to our national problem. The success of their work is due not only to their expert knowledge, but also to the fact that they have the complete confidence of their industries. It is difficult to see how similar results could be achieved by any agency other than a research association.

VII.—CONCLUSION.

As you know, D.S.I.R.'s task has been to influence industry—to influence its faith and its convictions—and to inculcate in industry the realization that research is the price of industrial progress. As a Government Department, D.S.I.R. has doubtless on occasion been the subject of suspicion in this connection. But once it has been realized that the Department's intention has been to be helpful, such suspicion, in the few cases where it has existed, has rapidly evaporated. In dealing with people I have always found two golden rules to apply. It is always best, at the start, to impute to people the qualities you would like them to possess. You then almost invariably find that they display those qualities. In any case, it is better to trust and be deceived than to distrust and be mistaken. Also I hope I shall not be accused of cynicism when I say that one can achieve almost anything if one is prepared not to want the credit of it.

It is in the latter connection that I wish to pay a tribute to the administrative staff of the D.S.I.R.—to the men and women who do not share the limelight associated nowadays with scientific discovery, or the headlines which announce striking technical applications. Much has been rightly said about the high qualities of both mind and character displayed by members of the British Civil Service. I leave it with a warm admiration for the traditions of loyalty and integrity which have been built up through the years; and I venture to add that no members of the Civil Service exhibit those qualities in more generous measure than do the administrative staff of D.S.I.R.

DISCUSSION ON PAPER BY MR. A. P. C. HALLOWES: "THE WORKING BEHAVIOUR OF PHOSPHORUS-DEOXIDIZED COPPERS CONTAINING BISMUTH." *

(*J. Inst. Metals*, this volume, p. 1.)

MR. E. A. BOLTON,† M.Sc. (Member of Council): I did not intend to discuss this paper at all, but I should like to pay a tribute to the very careful and painstaking work which has been carried out by Mr. Hallows and his colleagues. The paper is not really one for discussion, but I feel that it is certainly one which should be used for reference.

I was very glad that in his introduction the author emphasized a point which he made in the paper, namely the danger of re-embrittlement. In times of stress if we have to use these coppers, manufacturers would take very careful note of the procedure required in order to render the high bismuth content less harmful; but when sheets or tubes reach the user, that point may not be sufficiently regarded. I can imagine that copper sheets or tubes may go out from the manufacturer in a perfectly good state, but when they get into the hands of the user the wrong treatment may be given. They may receive either too much cold work or the wrong form of heating. If we ever get into such a position again, I would emphasize the importance of the trade being very carefully briefed on the use of such high-bismuth coppers.

MR. T. W. COLLIER ‡ (Member): At the end of the paper the author tells us that severe cold work should be preceded by annealing at relatively high temperatures and quenching, the annealing temperature required varying with the bismuth content of the copper and the severity of the working operation. He then goes on to say: "For example, severe cold work should be preceded by annealing at and quenching from 650° C. for material containing up to 0.0025% bismuth, and 750° C. for material containing from 0.0025 to 0.007% bismuth". It will be very difficult for manufacturers to quench from that temperature, and I should therefore like to know whether we can quench from a lower temperature or must we still go higher in the annealing.

In the report of drawing behaviour in tube manufacture, it appears that most of the trouble is experienced in tagging which is, as we all know, a very severe cold-working operation. As manufacturers I think we should probably try to overcome that by some other form of pointing, and I should like to know whether, say, push pointing would have eliminated that trouble, and had this work been done with push pointing, whether the author would have recommended still higher bismuth content.

MR. T. HENRY TURNER,§ M.Sc. (Member): The biggest use for phosphorus-deoxidized copper may be in fire-box plates, and I should like to know whether

* Discussion at the Annual General Meeting, London, 30 March 1949.

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the author recommends any alteration in the now specified limits of arsenic and bismuth, as the traditional addition of arsenic has an influence, and fire-box plates require both hot and cold working.

MR. V. B. Hysel,* M.Sc. (Member): There is one small point which I should like to add concerning the use of coppers containing bismuth in wire production. It occurs to me that the annealing of any fine wire at high temperatures may be difficult or even impossible owing to the sticking together of adjacent strands.

THE AUTHOR (*in reply*): I should like to thank the four speakers who have commented on the paper, and particularly Mr. Bolton for his kind remarks about the work.

Mr. Bolton also spoke of the possibility of re-embrittlement of the copper in the hands of the user during subsequent heat-treatment and working operations. The flattening and doubling-over tests on tubes annealed at temperatures lower than those used during manufacture (Section V) emphasize the danger of this re-embrittlement, and manufacturers can clearly only adopt these recommended annealing procedures with coppers of high bismuth content when the products are such that no subsequent heat-treatment is likely to be necessary by the user.

Mr. Collier asked whether the annealing temperatures of 650° and 750° C. advocated in the practical recommendations of the paper are also important at the instant of quenching or whether some drop in temperature is permissible. These recommendations are based on the works trials described, in which about 100° C. difference occurred between the temperatures of annealing and quenching, and latitude of this order must be permitted in any normal industrial-scale operation. It will be advantageous, of course, to minimize the difference between the temperatures, and this assumes greater importance as the severity of subsequent working operations is increased.

Since a proportion of the failures in tube drawing occurred during tagging, it is likely that a less-severe operation such as push pointing would raise the bismuth limits to some extent. The present work was not concerned with push pointing, however, and it is not possible to estimate the bismuth limits which would have been obtained using it. The severity of the tagging operation should have resulted in defining the highest permissible bismuth limits for tube drawing.

In reply to Mr. Turner, both arsenical and non-arsenical coppers were used in this work, and although the results obtained were not entirely consistent, there was, for the same bismuth content, little difference between the degree of embrittlement in the two varieties of copper. The results obtained do not call for any alterations to be recommended in the arsenic and bismuth limits of the existing specification relating to locomotive fire-box plates.

Mr. Hysel remarked on the possibility of wire products sticking if the high annealing temperatures recommended were employed in practice. This difficulty can best be overcome by single-strand annealing in a continuous furnace.

CORRESPONDENCE.

MR. CLEMENT BLAZEY,† M.Sc., B.Agr.Sc. (Member): I have followed the various investigations by the British Non-Ferrous Metals Research Association

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on the effect of bismuth in copper with much interest. My own work on the subject was begun so long ago that, like a lady of uncertain summers, I now recoil from any reminder of it. There will be general agreement that, in recent years, the B.N.F.M.R.A., with the co-operation of Imperial Chemical Industries Ltd., Metals Division, have made this subject notably their own.

The present series of investigations has, of course, been fully justified from a practical aspect through the use of certain types of South African blister copper containing bismuth, and it has been so thoroughly carried out that little, if any, trouble is likely to arise through the use of these or any other types of copper containing bismuth, but, twenty-three years ago; when the bismuth problem was more obscure than it is to-day, trouble arose at Port Kembla through the use, in refinery charges of arsenical copper, of scrapped locomotive fire-boxes and stay-rods composed of bismuth-bearing tough-pitch copper fabricated in the early years of the century. That early locomotive copper was likely to contain a relatively high percentage of bismuth is indicated by analyses quoted by L. Archbutt in an address in 1912 to the Birmingham Local Section of the Institute of Metals.*

The arsenical copper that provided the material for the original investigation in 1925 was deoxidized with phosphorus prior to casting, but it is likely that the use of an unusually high proportion of tough-pitch copper in the furnace charges upset the normal refining operation to the extent that there was probably too high a proportion of oxygen in the charge at the time of casting and, hence, a higher proportion than usual of oxide to be reduced by the added phosphorus. As a consequence, there was probably insufficient residual phosphorus to neutralize the embrittling effect of the bismuth in the billets. This, at any rate, was ultimately thought to be the explanation of the trouble, and the practical solution was to control the quantity of scrap and pay closer attention to poling and deoxidizing operations.

In a book written by—if I remember correctly—Professor F. J. Soddy, I once came across the sentence "A problem solved is dead", but this bismuth in copper problem points to the truth that he would be a very wise man who could say when a problem is finally solved. The farther one goes the farther one has to go.

It has for long been apparent to me that the greatest uncertainty in the original investigation lay in the exact chemical composition of the billets. The introduction of a precise colorimetric method for determining bismuth by the Fiscal Policy Technical Sub-Committee of the Brass and Copper Industries in 1933 † and the further work on this subject by C. O. Bannister and W. M. Doyle in 1935 ‡ was of great assistance in my later investigations, as no doubt it has been throughout those conducted by the B.N.F.M.R.A.

A factual paper like this recent one by Mr. Hallows leaves little room for critical comment and plenty of room for commendation, if that were necessary to a scientific investigator.

All that I, for one, can suggest is that, if the B.N.F.M.R.A. is prepared to go farther, there remain for investigation the precise effect of oxygen on bismuth brittleness, not neglecting the effect on low-oxygen bismuth-bearing copper of exposure to air during pouring, and the effect of elements, such as nickel and, possibly, iron, which can combine with phosphorus to render nugatory its beneficial effect on brittleness. The former suggestion may appear to be of academic rather than practical interest, as no one is likely to cast low-oxygen bismuth-bearing copper, but the latter suggestion may in the end have a practical bearing since one sometimes succeeds in turning a bad

* *J. Inst. Metals*, 1912, 7, 262.

† See, for example, *Metal Ind.* (Lond.), 1933, 42, 538.

‡ *Metal Ind.* (Lond.), 1935, 46, 96.

thing to good use. Bismuth brittleness might, if properly controlled, lead to the development of free machining properties and, when associated with precipitation-hardening through the presence of other elements, provide a high-strength alloy of the free-machining type. I had this as one objective in some work I carried out in 1943-44,* but for various reasons I was unable to complete the investigation. A solution to the problem has been found by others in the use of a sulphur-nickel-phosphorus-copper alloy,† while, in the U.S.A., I fancy that tellurium has been used in place of sulphur. Sulphur, selenium, and tellurium are, of course, the additions that one would expect to find in free-machining alloys.

No doubt, Mr. Hallows and his co-workers could suggest other more interesting extensions to the bismuth problem.

The AUTHOR (*in reply to correspondence*): We appreciate the remarks by Mr. Blazey, and it is gratifying to find that he, as one of the pioneers of work on the effects of bismuth in copper, has followed the Research Association's work so closely.

The accurate determination of bismuth contents has been essential throughout our research on this subject. Two methods have been used, one essentially the same as that mentioned by Mr. Blazey and the other due to Fitter,‡ which, while using a different separation of interfering elements, is finally dependent upon the iodide colour for its result. Accuracies of the following order are obtainable:

$$\begin{aligned} &\pm 0.00005\% \text{ on contents up to } 0.001\%. \\ &\pm 0.0001\% \text{ on contents over } 0.001\%. \end{aligned}$$

The Association's research on bismuth in copper has now been concluded, but before the work ended a short investigation was made into the embrittlement of tough-pitch copper by bismuth, and these results will be published shortly.

* *Proc. Australasian Inst. Min. Met.*, 1944, [N.S.], (135), 65.

† *Metal Ind.*, 1947, 71, 301.

‡ H. R. Fitter, *Analyst*, 1938, 63, (743), 107.

DISCUSSION ON PAPER BY MR. T. HOWARD ROGERS: "THE PROMOTION AND ACCELERATION OF METALLIC CORROSION BY MICRO-ORGANISMS." *

(*J. Inst. Metals*, this volume, p. 19.)

MR. T. HOWARD ROGERS (*presenting his paper*): In introducing this paper there are one or two points that I should like to emphasize.

In the first place, the fact that micro-organisms can play a part in the corrosion of metals is no longer the novel conception that it was when this work was first contemplated. There are now many references throughout modern literature to the effects of bacteria which have had to be taken into account both in practical failures and in laboratory experiments. Some of the ways in which bacteria and moulds can affect corrosion reactions are set out in my paper, but the whole field is by no means covered. Many corrosion investigators, particularly some of the American workers, are studying cycles other than the well-known sulphate-to-sulphide reaction and the mercaptan-disulphide reaction described in the paper. So many chemical reactions are associated with micro-organisms (particularly those of the reversible oxidation-reduction type) that there can be few corrosion environments where the possibility of some biological action affecting corrosive attack can be dismissed.

The effect of micro-organisms upon corrosion reactions, however, is still likely to be overlooked, and I think two points need touching upon. Firstly, there is the extreme localization of the production of corrosive substances in the case of a bacterial colony or bacterial slime associated with a metal surface. This makes it improbable that any general examination of the corrosion environment will reveal any quantity of the corrosive agent, particularly if the location is in flowing water. Secondly, in the case where the products of bacterial metabolism generally infect the medium surrounding the site of corrosion activity, the amounts of corrosion accelerators necessary to increase attack are often so small that they are quite unlikely to be detected in normal methods of examination, for instance, standard water or soil analyses. As an example of this, it has recently been found that sea water containing an amount of hydrogen sulphide undetectable by the normal alkaline lead acetate test is still extremely corrosive to copper-base alloys, and further within certain limits the lower the concentration of hydrogen sulphide the more severe the acceleration of attack.

It is perhaps necessary to call attention to the unusual copper tolerance of many of the bacteria examined. This tolerance has been confirmed by many other workers, especially those investigators interested in anti-fouling paint, &c.

I should also like to call attention to the extreme variability of sea water as a corrosive medium. Great lack of reproducibility is often experienced in corrosion testing in sea water, and there is little doubt that this is due to the many ways in which the bacteria in any sample of sea water can affect the character and amount of the organic compounds present. It must be pointed out, however, that the effect of the bacteria is not necessarily accelerative,

* Discussion at the Annual General Meeting, London, 30 March 1949.

since it is possible for the products of metabolism to yield substances with film-forming properties which may inhibit corrosion.

With regard to the presence of cystine in sea water, since it has been shown experimentally that organic sulphur compounds can act as corrosion accelerators, many sea waters have been examined for the presence of these substances, and although the amounts present are very often extremely small, sea waters have been found which on receipt in the laboratory have been positive to the usual tests for organic sulphur compounds.

In experiments conducted with cystine and glutathione it should perhaps be pointed out that the behaviour of these substances is most variable unless the experiments are conducted under strictly sterile conditions. Some sea waters appear to contain bacteria which are able to break down these substances and acceleration of attack does not continue unless the concentration of the organic sulphur compounds is maintained.

It is only necessary to refer briefly to the sulphate-reducing bacteria, but with regard to non-ferrous metals these bacteria can be quite as dangerous as they are to ferrous materials, although the reaction is possibly due more to the inorganic hydrogen sulphide than the sulphate-sulphide metabolic cycle of the bacteria.

I would call attention to the possible break-down of paraffin wax by bacteria in corrosion experiments. Many more cases have been noted since the original experiment quoted, and I feel that a definite warning might be given against the use of this material in corrosion experiments.

The methods of control of corrosion due to bacteriological action will, of course, depend very much upon the particular case where control is necessary. Where the corrosion environment is sufficiently small for economic treatment with some form of bacterial inhibitor this type of control can be, and has been found to be, very successful. Often, however, the environment is too large and the cost of suitable inhibitors too great for such use; in these instances it would appear that the best solution is the use and development of alloys which form films resistant to contaminating substances.

In conclusion, I should like to apologize for two typographical errors. On p. 27 the cystine-reaction equation should have a dot or plus sign after the H to signify that hydrogen ions are concerned, and in the references Mr. Bunker's initials are reversed—they should be "H. J." and not "J. H."

DR. U. R. EVANS,* F.R.S (Member): I should like to congratulate the author on this valuable paper. Mr. Rogers is a real enthusiast, and his work has revealed matters of great practical and scientific importance.

The paper is a micro-biological one. I am not a micro-biologist and possibly I should not be discussing it. But there are different kinds of micro-biological action. For instance, Mr. Rogers, speaking of the activities of the sulphate-reducing organisms, writes of the corrosion reaction as being "an integral part of the metabolic cycle of the bacteria". He would be a rash man who, without a knowledge of bacteria, started to discuss such matters, and I do not propose to do so. Later, however, Mr. Rogers states that cystine is contained in many tissues and can be released by bacterial action. If once we accept the release by bacteria, the cystine should behave in much the same way as cystine purchased from the chemical dealer; consequently, the layman is entitled to discuss its action. It is still necessary, however, to be careful, because Table I shows a comparison between cystine (sterile) and cystine (non-sterile), and the effects are by no means identical.

It is suggested—and I accept the suggestion—that cystine forms over the greater part of the brass surface a coat which acts as a cathode, while the un-

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coated surface acts as anode; presumably the coating is not cystine itself but some copper derivative. The combination of a large cathode and small anode will lead to severe attack on the latter. It is suggested that the cathodic reaction reduces the cystine to cysteine, taking up hydrogen, and that oxygen dissolved in the water restores the cysteine to cystine; the film-substance is in effect an oxygen carrier, or at least an oxygen utilizer, enabling the oxygen to act indirectly as a cathodic stimulator; that can only occur if the film substance possesses electronic conductivity, because the electrons must pass through the coating if the cathodic reaction is to take place.

Corrosion in these circumstances is only likely to be intense if the cathodic area is large compared with the anodic area. Many analogous cases are known, such as that of iron carrying mill-scale broken up by small gaps. Much oxygen can reach the large cathode, producing considerable electric currents (which have been detected); the whole effect of such currents will be concentrated on the small anodes (the exposed iron). Thus one gets dangerous pitting where otherwise one would get harmless general attack. In the case of cystine, the most dangerous conditions will occur when the film covers the greater part of the surface, but, either because the amount of cystine is insufficient or because there is impingement on some particular point, there is a small bare anodic area. Such a combination must lead to intense attack. Evidently cystine is particularly dangerous under impingement conditions—a point of practical importance.

Mr. Rogers reasonably regards cystine as a provoker of corrosion, but it presents analogies to bodies which are classed as dangerous inhibitors. An iron specimen placed in sodium chloride solution suffers considerable corrosion, which is generally well spread out so that there is no rapid loss of thickness. If sufficient sodium carbonate is added, corrosion can be stopped altogether; if, however, the quantity added is insufficient, corrosion is restricted to small areas, leading to the combination of small anode and large cathode, so that there is intense attack. It has been found in laboratory experiments and also in practice that under such conditions the local loss of thickness is enormously greater than if no inhibitor had been added at all, although the total corrosion is considerably reduced. That a rather similar state of affairs exists in the case of cystine is shown in Fig. 4. If enough cystine is present there is ultimately less corrosion than if no cystine is present, but the intensity of corrosion may be greater in the presence of cystine than in its absence.

It may well be objected that pitting cannot be cured by conferring on the pitting agent a more pleasant-sounding name. That is true, but it is well worth noting that in some respects cystine behaves as an inhibitor—as indeed Mr. Rogers has stated—since it might be possible to take advantage of the fact in reaching a cure. The *primary* action of the cystine is to produce a film which will *stop* corrosion where the film *exists*; the *secondary* effect is to produce very *intense attack* at the place where the film *does not exist*. Is it possible to use the primary effect without producing the objectionable secondary effect? I am not sure, but it would be interesting to try the effect of water containing cystine along with a zinc salt. It is likely that we should get the cystine film and on top of that a film of zinc hydroxide might be deposited as a cathodic product. This might inhibit the cathodic action and, although corrosion would doubtless continue at the breaks in the film, it should not be more intense than if there was no film present at all. In the case of iron, zinc sulphate is known to cause much less corrosion than sodium sulphate, owing to the formation of zinc hydroxide as the cathodic product.

It would be interesting to try some experiments on these lines in the laboratory, because, if they did nothing else, they would increase our grasp of the situation. Of course, it might be found that zinc salt precipitated the cystine, and if so it would suggest another possible way of overcoming the

trouble. If the experiments provided a cure which was effective in the laboratory, the question would arise as to whether one could use the same principle for preventing trouble under service conditions. It would be very interesting to hear Mr. Rogers's opinion on these matters. If it were decided that zinc salts were the correct remedy, it is obviously not going to be very easy to apply them. One might consider, at least for troubles occurring at the inlet ends of the tubes, whether the application of a metallic zinc paint might not be worth-while. As long as the zinc survived, it would furnish a large anode, and prevent the dangerous combination of large cathode and small anode. Although it might not last very long, it would, I think, tend to deposit zinc oxide on the parts which would otherwise be potential cathodes, and might leave a state in which the objectionable chain of developments would not subsequently be set up.

Some sort of cure of that kind would be welcome, since the cures based on dyestuffs may not be universally applicable. One knows of cases where really wonderful effects have been produced by the dyestuffs advocated by Mr. Rogers, but presumably there are circumstances under which they could not be used. For instance, where cystine liberated by bacterial action is present throughout the water of a harbour, one could not pour into the harbour gentian violet on the required scale. Consequently other possible cures deserve to be considered, although possibly the one suggested above may have to be rejected.

DR. F. A. CHAMPION,* A.R.C.S. (Member): Mr. Rogers's experiments showing the important effects of micro-organisms and their products on corrosion in sea water are of wide interest, since they affect the complex question as to the most satisfactory corrosive medium for laboratory tests intended to simulate marine conditions. It is usually desirable in laboratory tests that the corrosive employed should closely resemble that to be met with in service. Mr. Rogers has provided still more evidence of the complexity and variability of sea water, not only in the natural condition, but especially when one tries to use it in a laboratory, away from its natural environment. Although one can get sea water taken well out at sea, it does not really provide the answer to the problem.

Dr. Evans has pointed out that the elimination of the effects of these micro-organisms by sterilization or the addition of dyes does not provide a practical method of avoiding corrosion in service, and Mr. Rogers has stressed that the practical answer in this respect is to develop alloys which will stand up to these conditions. The development of these alloys would be much easier, however, if one had available corrosive media with which one could get reproducible results and which did represent the natural corrosive. That difficulty in getting reproducibility—and, of course, the convenience of simple inorganic solutions—has led many people to use either sodium chloride solution or a more complex inorganic solution such as that developed by Whitby,† although it means some departure from the natural conditions.

I should like to ask Mr. Rogers what hope he can hold out for improving on that state of affairs. Is it possible to develop solutions which will represent the natural conditions in a reproducible way? For example, is it possible to control the action and the products of the micro-organisms in a natural sea water, or is it better to start off with the synthetic solution and add organisms or constituents to obtain a suitable corrosive medium?

It is a complex question, because sea water varies naturally and therefore a single, universal solution cannot be expected. The open sea, estuarine

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† L. Whitby, *Trans. Faraday Soc.*, 1933, 29, 523.

waters, harbour waters, and so on, should be represented, and the medium should be applicable to a wide range of metals. I think any progress Mr Rogers can make in that direction would be widely appreciated.

There is one other question I would like to put. It relates to the division of bacterial action into three classes on p. 20. The first refers to corrosion that can be brought about "by direct action, for example by the production of corrosive substances such as carbon dioxide". The third class refers to corrosion "in cases similar to the anaerobic corrosion of iron, by the activities of the sulphate-reducing organisms, where under some conditions the corrosion reaction is an integral part of the metabolic cycle of the bacteria". As a layman, it seems to me that the latter is a more direct action than the former. If Mr. Rogers could enlarge on that point it might be helpful.

MR. T. HENRY TURNER,* M.Sc. (Member): I should like to ask whether the bacteria-accelerated reactions the author has studied produce localized or general corrosion under practical service conditions. Many years ago this Institute was interested in the sea-water corrosion of brass, and Dr. Bengough studied that for many years. Shortly before he died, he was Chairman of the Marine Corrosion Sub-Committee, which was more interested in iron and steel. The anti-fouling problem was linked with corrosion, because it was found that fouling and corrosion occurred associated with one another.

Throughout the world sea waters vary in composition. Fouling was negligible when ships were running at sea and occurred in or near harbours. In these early tests one used to get a barrel of sea water, send it to the laboratory, and feel happy that one had the genuine article. But there is not a single genuine sea water: the Baltic and the Mediterranean differ in density from the Atlantic and the Pacific. The Amazon, the Hudson, the St. Lawrence, and such great rivers run very far out into the ocean. So one must almost define the location and the time and temperature when speaking of sea water for corrosion tests. That is an awkward complication, however, and I think these micro-biological effects would be mainly located in coastal waters.

Another matter that came to the attention of the Marine Corrosion Sub-Committee was the extraordinary difference in the behaviour of steels when one considered weight loss. The highly resistant stainless steels, high-chromium; and high-chromium and -nickel steels do extraordinarily well, but they pit and fail locally which makes them sometimes unreliable from the engineer's point of view.

On the other hand, some of the "low-alloy" steels (with, say, 1% chromium and 1.5% manganese; and, if I remember rightly from the work that Messrs. Hadfields put at our disposal in those days, 2½% chromium was one of them) did not suffer from localized corrosion and gave good service. I would suggest that the same applies to non-ferrous materials. The engineer or other user is less interested in loss of weight by corrosion than in the loss of weight by corrosion concentrated in one part of his component.

I observe as an interesting feature of metallurgy that, generally speaking, non-ferrous materials resist corrosion and return into use as secondary metals much better than steels, which leave a great weight of unrecoverable iron oxide strewn about the earth.

DR. E. VOCE,† M.Sc. (Member): I should like to add to what Mr. Turner has just said that it is not only the engineer who is interested in localized corrosion: it is also the plumber.

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† Chief Metallurgist, Copper Development Association, Radlett, Herts.

May I ask Mr. Rogers whether he thinks that the deep type of pitting which is sometimes a menace in ordinary water systems could be attributed to biological action. It has not been thoroughly explored, I know, and work is going on, but the sooner we can reach a solution of this very important problem the better.

MISS DOROTHY PILE * (Member): I am taking courage from the fact that Dr. Voce has mentioned plumbers, to go a little further and mention cooks. I find that there is a tremendous amount of corrosion in an ordinary kitchen—and local corrosion at that. One does use an astonishing amount of salt water in a kitchen. In cooking vegetables, and most other foods, one adds a certain amount of salt to the water and, though I do not suppose it corresponds to sea water, it is still a saline solution and a varying one at that. I do not know whether it is the sign of a good or a bad cook, but the amount of salt put into water to be boiled is seldom measured and mostly varies from a handful down to a teaspoonful. I have noticed that this varying solution combined with different vegetables has a definite effect on the surface of metal saucepans, and aluminium in particular. If a cauliflower is boiled in a new saucepan a peculiar film is left afterwards from the water and with a cabbage the film may be quite different. I have found that one of my most necessary kitchen implements is a lens; and I fear that my culinary efforts are often spoilt through being combined with corrosion research.

I was amazed to see, after ten years' constant use, the pitting effects on an ordinary aluminium pie-dish; and this had only been used for such ordinary dishes as meat pies, milk puddings, and so on.

If these corrosion experiments are being undertaken I think the cooking side of it should be looked into very thoroughly indeed, as it certainly affects the housewife. I have been greatly interested in this subject, and I have often wondered whether there is such a thing as what I can only describe as "stabilized" corrosion—that is, corrosion to a certain extent and then an apparent stoppage—which is what you so often find in cooking utensils. To start with a certain amount of film, top surface, &c., is removed and then stabilization is reached. I have not really gone into this very deeply, but here is a fresh field that I would offer to the author of this very interesting paper.

MR. P. T. GILBERT,† B.Sc. (Member): I should like to make some response to Mr. Turner, who has asked whether the corrosion due to micro-organisms in Mr. Rogers's work is local or general. The attack is, often, very much localized and therefore dangerous.

Much of Mr. Rogers's work has been in connection with corrosion in ships' condenser systems, and for this research the standard test used by the B.N.F.M.R.A. is the jet-impingement test which was developed by Mr. May. The effects of contamination in sea water are remarkably shown up in this test. With a specimen of copper alloy which is subjected to impingement by a jet of sea water containing air bubbles, it is possible to get complete penetration at the jet area in a contaminated sea water in a four weeks' test, whereas with the same alloy in a clean sea water the attack may be hardly measurable. This sort of effect is closely connected with contaminating substances produced by bacterial action.

The highly localized attack in this particular test is, as Dr. Evans explained, due to the production of an "artificial" anode where the protective film is broken

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down by the action of air bubbles breaking on the surface of the specimen. Surrounding this anode are large areas behaving as efficient cathodes because of a good supply of oxygen from the moving aerated sea water. There is, however, another type of localized attack which can occur in contaminated waters in this test, apart from that at the jet. Local breakdown at blisters in the film with consequent quite deep pitting can occur all over the specimen in contaminated waters.

It does seem possible, however, for general or over-all corrosion in sea water to be accelerated by contaminating organic substances in some circumstances, although I am not sure what the mechanism is.

Fig. 4 (Plate II) in Mr. Rogers's paper, giving the loss of metal against time with varying amounts of cystine, shows that in the later stages of the test the cystine additions are inhibiting attack. Dr. Evans has rightly pointed out that the cystine is in some respects behaving similarly to an anodic inhibitor. But in the early stages of the test there is an acceleration of attack proportionate to the amount of cystine added, and this fact has been used to estimate the corrosiveness of sea waters.

I am anticipating a future paper by Mr. Rogers in mentioning this point, but it is relevant in this connection. A piece of pure copper is suspended in a beaker containing sea water under standard conditions for a day and the amount of copper that has been corroded away is estimated. The results have proved to give a very good indication of the corrosiveness of a sea-water sample, but the interesting point is that under these conditions the attack is almost always general. In some way, therefore, the organic substances can increase general corrosion as well as producing under other conditions much more dangerous localized attack.

I would mention in passing that this test shows that the corrosiveness of sea waters towards copper can vary by a factor of five or six. In that respect I sympathize with Dr. Champion's plea for a more reproducible sea water for use in corrosion testing. We at the British Non-Ferrous Metals Research Association are very conscious of the need for such solutions, which we are endeavouring to produce both by using synthetic solutions and by modifying the characteristics of natural sea waters.

In that connection, I should like to know whether there is any evidence that variations in the properties of sea water cause variations in the corrosion of materials other than copper alloys, for instance, aluminium alloys. While there is much evidence in the case of copper, very little work seems to have been done on aluminium alloys, and I do not know whether biological action is a factor that has to be taken into consideration in the case of aluminium.

MR. E. I. BRIMELOW,* M.Eng. (Member): I have read Mr. Rogers's paper with great interest, since I have been particularly interested, on the ferrous side, in the corrosion of buried steel pipes. I should like to ask Mr. Rogers whether he has any information on the possibility of copper pipes and zinc-coated pipes suffering from attack by these micro-organisms. It does appear that another important factor has been identified in the field of corrosion.

Dr. Evans and other investigators have pointed out on numerous occasions the various factors which play a part in the corrosion of metals, and now we are faced with this new factor, the influence of bacteria, which seems to complicate this field of investigation still further. It is revealed by what Mr. Rogers says in his paper that there is still a vast amount of work to be done before the whole position can be clarified. I think there is a danger, possibly, in rushing to micro-organisms as an explanation for all corrosion failure.

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There is one problem which has been puzzling me, and that is the problem of corrosion of aluminium water-service pipes. Aluminium, even when of a high purity, or as an alloy which is normally highly resistant to corrosion, is not at all suitable for this application. It may be, however, in this case, where the maintenance of a continuous film of oxide is so important for protection, that the living organisms present in certain waters may have some effect in producing the severe localized corrosion which occurs.

In conclusion, it does appear that metals which already suffer from fatigue ageing and from internal stress are now prone to another human ailment, namely, attack by micro-organisms and bacteria, a scourge which may prove as troublesome as the common cold.

DR. H. J. AXON,* B.Met. (Student Member): I was glad to note that the last speaker indicated how complicated a field this is. For myself, I know very little about corrosion, but I have a great respect for those hardy spirits who tackle it.

We have, in the course of this discussion, heard how complicated matters are outside the corroded metal, and we have heard from Dr. Evans some of the complications on the surface of the corroded metal. It occurs to me that as metallurgists we might be interested to consider yet another factor—the complications which actually occur inside the metal. After all, it is particularly difficult to obtain a pure metal. In any case, one is generally dealing with alloys, which are as likely as not segregated, and even if all these factors are absent, there is still the possibility of localized mechanical stresses.

The question of grain-size presumably comes into it also, since one knows it may do so in the analogous case of the electrolytic etching of aluminium. One tends to get large etch pits at the grain boundary and smaller etch pits in the bulk of the grain. I hope that people who are interested in the complications in the present state of affairs will feel I have added something to these complications, and I would plead for a discussion of the metallographic condition of the specimen in all corrosion work.

DR. CHAMPION: I do not think the question of the effect of variations in sea water on aluminium alloys has been studied very intensively, and one would like to know more about it. There has certainly been difficulty in correlating results obtained in the sea with laboratory tests, but it is questionable to what extent this has been due to variations in the sea water.

I am aware of no evidence that micro-organisms have played a part in the corrosion of aluminium, but again there is plenty of room for work on that question.

THE AUTHOR (*in reply*): I must thank the many speakers who have contributed to the discussion, which has ranged from cooking through plumbing to condenser tubes, but I hope that they will not expect me to answer everything at this moment. Some of the points raised will undoubtedly have to be dealt with in correspondence.

To answer one question out of order, some people are rather worried that the biological aspect of corrosion is unduly increasing the number of variables and think that we are introducing even more trouble into corrosion tests. This I think, though unfortunate, is probably the case, for I am certain that biological factors must be taken into account to obtain a true picture of some corrosion problems.

I must thank Dr. Evans very much indeed for his introduction of the

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discussion and his complimentary remarks. I am very interested in the question of cystine acting rather like an inhibitor—a dangerous inhibitor—and I am sure my colleague Mr. May will also be interested, as he has also called my attention to this resemblance. I think it is true that the cystine can work in that way, but I would make one point. Increase in the amount of cystine present does not necessarily decrease the corrosion by the formation of thick films which blanket impingement attack, such films being very liable to blister and break-down with encouragement of pitting action.

With regard to the zinc salts I shall certainly keep that suggestion in mind. It is true, of course, that in practical conditions copper salts and iron salts do help in limiting the amount of attack which may occur as a result of the presence of cystine. They have the effect of absorbing the cystine out of the solution. We have shown experimentally that it is possible to remove cystine from sea water by the addition of iron salts.

I do not think dyestuffs could be used to inhibit the action of cystine, but they certainly might be used to inhibit the bacteria which produce the cystine.

I very much appreciate Dr. Champion's wish for a standard sea water, and all workers in sea-water corrosion problems will echo his desire. At the same time, we are not at all sure what a standard sea water should be. Should it represent estuarine water, harbour water, or open sea water? We have already tackled this problem and, as has been pointed out, we hope eventually to be able to make a standard sea water which will produce the required standard attack. We can then correlate that attack to that of the least corrosive and most corrosive sea waters.

The classification on p. 20 was only a rough one, and I had in mind that some substances once produced by bacterial action could then give a direct chemical attack. In the other instance the attack is more indirect, the cathode of the corrosion cell being depolarized, in the case of the sulphate-reducing bacteria, as an inherent part in the cycle of the bacteria's own life. The bacteria which develop in anaerobic conditions use the cathodic hydrogen in reaction with organic matter to obtain energy. It may be that I did not phrase the passage very well.

With regard to steels, localized corrosion could, of course, be accelerated by substances produced by bacterial action, and the same would apply to general corrosion of ferrous materials. One reason why cystine in particular has been studied is because it has been shown to be capable of considerably accelerating the local corrosion of copper-base alloys, and in condenser tubes localized corrosion is very much more important than generalized corrosion.

Dr. Voce wonders what we are doing about deep pitting of copper. Considerable research in this problem is taking place, including the effect of micro-biological reactions, but I would not wish to go into it very deeply to-day.

Finally, on the question of cooking and corrosion, I would suggest that the failure of a condenser tube may be of more considerable moment than the failure of a cooking pot, and that this will no doubt account for the disparity of effort devoted to the two problems.

CORRESPONDENCE.

The AUTHOR (*in further, written, reply to the discussion*): I would like to add to my remarks on Dr. Evans's suggestion for the use of zinc salts as a means of combating the effects of cystine in sea water. It has been shown experimentally that zinc is not so effective as iron in removing cystine from sea water and, further, in certain non-ferrous alloys, especially those which form good protective films, like aluminium brass, the presence of zinc cor-

rosion products in the scales has been found to lower the normal high corrosion-resistance. For this reason, I think it would be unwise to advocate the presence of zinc salts in condenser systems, where the majority of the materials are non-ferrous, and in particular the replacement of iron protector blocks by zinc is not to be recommended. The use of zinc salts in a fundamental experiment would, of course, be a different matter.

In reply to Mr. Brimelow's query I have examined several cases of copper and galvanized steel where corrosion has been accelerated by the presence of hydrogen sulphide produced by bacteria. There is no evidence, so far, that the attack is of the same type as in the anaerobic corrosion of iron due to these organisms. The attack in the cases I have seen has been due to the direct action of the H_2S which may have been produced at some distance from the site of actual corrosion. I have no comments to make upon the possible corrosion of aluminium by micro-organisms as little work has been done in this field.

In reply to Dr. Axon I entirely agree that in any corrosion investigation consideration must be given to the internal complications of the material, a point generally recognized by corrosion investigators. Cases where corrosion is due to physical factors both internal and external to the metal are far more numerous than those which have a biological explanation, and in many cases they are better understood.

DISCUSSION ON PAPER BY MR. H. BURDEN AND MR. A. BARKER : " THE MEASURE- MENT OF GRAIN-SIZE OF TUNGSTEN AND TUNGSTEN-CARBIDE POWDERS USED FOR THE MANUFACTURE OF 'HARD-METAL.' " *

(*J. Inst. Metals*, this volume, p. 51.)

MR. A. E. OLIVER,† F.I.M. : It is a great pleasure to me to open the discussion on this interesting paper, although I cannot claim to have any special knowledge of grain-size measurement techniques. At the same time, the subject is of great interest to me, as I am sure that it will be to others engaged in the powder metallurgy industry. Of all the various process-controlled tests which are regularly used in the hard-metal industry, there is always a certain amount of doubt concerning the results of grain-size measurement of tungsten powder. Most companies pass through a phase in which several possible methods of measurement are explored, and then one particular technique is adopted which is considered sufficiently sensitive to enable proper control to be exercised over the production of tungsten.

Under good production conditions, most of the works' samples will regularly fall between the limits of grain-size laid down by the laboratory after the exploratory work has been carried out. For a time all is well, and then one day something seems to go wrong; a batch of powder, the grain-size of which has been found to be well within the specification, produces a sintered hard-metal of abnormal grain-size. Such occurrences happen from time to time, and the most careful investigation seldom provides any satisfactory explanation. Finally, one is forced to conclude that there is obviously something fundamentally wrong with the method of grain-size measurement. Other methods are tried, but are usually discarded one by one as their respective weaknesses become apparent. For this reason, any serious attempt to investigate thoroughly the subject of grain-size measurement in the range of interest to the hard-metal industry must be welcomed, and the authors are to be congratulated on their paper on what is admittedly a very difficult subject.

On reading the paper, I observed that in all the methods tried the usual difficulties in dealing with aggregates have been experienced. There is little doubt that, unless something can be done to overcome this trouble, no method of grain-size measurement can ever be anything more than a very rough indication of particle size. Under such conditions, a test is far from reliable and indeed can often be misleading.

Another factor of undoubted importance is the measurement of particles below about $0.2\ \mu$. Such particles, when present, play an important part in grain growth during final sintering, and unless this fraction is included in the measurements the later behaviour of the powder cannot be accurately foretold. In many of the usual methods of measurement such fine particles are ignored, or the figures obtained are of doubtful accuracy.

For the purposes of their work, I noticed that the authors selected four types of tungsten metal powder of relatively widely different particle sizes.

* Discussion at the Annual General Meeting, London, 1 April 1949.

† Hard Metal Tools Ltd., Coventry.

The differences are so great that I am sure that apparatus of a very simple nature, such as that used for apparent-density determinations, would have been sensitive enough to identify the four types of powder used. Since the powders chosen differed considerably in particle size, the sensitivity of the various techniques employed has not, to my mind, been well-established, and the work might have been extended with advantage by testing a larger number of different samples of one type of tungsten. By this means it should be possible to decide the suitability or otherwise of any method for process control.

Furthermore, a study of the structure of the sintered material produced from the powder, such as the average grain-size, would provide useful information for correlation with the grain-size of the original powders. Evidence of grain growth may indicate a wide grain-size distribution or an excessive proportion of particles below about $0.5\ \mu$.

I notice that the authors are at present using the Spekker method for process control, together with occasional microscopic examination of the powders. In the circumstances, I am inclined to agree that these methods are probably as good as any, but I am wondering just how much reliance can be placed on the results obtained, and I should be interested to know the views of the authors on this point. In my experience, all the usual methods of grain-size measurement are so imperfect that only very serious departures from standard processing conditions in a works or the use of a different type of raw material are revealed.

The technique which appears to show most promise is electron microscopy, but for various reasons it does not seem possible that in the present stage of its development it will be suitable for the routine control of particle size. The behaviour of tungsten powder when made into hard-metal may depend not only on the actual size of the particles but also on their state of aggregation—that is, whether they are single- or poly-crystalline. With the possible exception of the electron-microscope technique which has been recently described by Delisle,* there does not seem to be any simple way of investigating this point. I should like to know whether the authors can throw any light on this matter.

The subject of grain-size measurement is so abstruse that one could discuss this valuable paper at great length. I am sure that its publication will be of benefit not only to manufacturers of hard-metal but also to workers in other fields whose problems are similar.

MR. E. H. S. VAN SOMEREN,† B.Sc. (Member): I am very glad that this paper is being discussed, because this is a problem which has given me, as well as others, some trouble. I think that it really calls for the help of an organic chemist, as well as of metallurgists and physicists, because the question of aggregation in metallic powders is closely linked with some of the problems of surface activity associated with flotation. I should like to offer the suggestion that ethylene glycol and its series of associated compounds, which have a rather higher viscosity than water but which have hydroxyl groups, should be used as the suspension agent. We have found for some metallic powders that diethylene glycol is quite satisfactory as a suspension agent.

I have another suggestion, and that is that if you cannot get all your compounds in a uniform state of surface activity—and that is the trouble with metallic powders; they do turn out with different states of surface activity—there is something to be said for adopting a quite different method, which is to follow the gain in weight when heating in oxygen on a semi-micro scale. A small quantity of these fine powders can be heated in oxygen, and the gain in

* J. Delisle, *J. Metals*, 1949, 1, (3), (III), 228.

† Research Assistant, Murex Welding Processes Ltd., Waltham Cross, Herts.

weight should be characteristic of the specific surface, in just the same way as the optical density.

MR. A. BARKER (*in reply*): Dealing first with Mr. Oliver's remarks, and with regard to his comments on exceedingly small particles, of less than 0.2μ or so, we agree that the problem there is quite difficult, and reasonably accurate and reliable methods for measuring that size-range are almost non-existent. It is only by the use of the electron microscope that one can get any real idea of what the nature of this type of particle is. I believe that it is possible with the air-permeability methods to get somewhere with these particles, but we have not tried that method yet.

His second point was that the four powders which we have used in the work described in this paper are widely different in particle size. The reason we chose them was in order to establish a relationship between particle size and hardness of the finished hard-metal, and they were selected so that any inaccuracy in particle-size measurement would be overshadowed by the wide variation in actual particle size, thus making it easier to get a definite correlation between particle size and hardness. We have actually used the Spekker method as a routine control for one of these types of tungsten, and it shows up small variations in size and can be used successfully for that purpose. As Mr. Oliver says, the apparent density of these four types would be quite different, and would easily show the relative grain-size, but that method cannot be used for a single type of tungsten on a production scale, which is being produced in a regular manner.

I think that we can answer his point about the reliance to be placed on the results by referring to Table VIII, in which we give the standard deviation of 8 specific-surface readings obtained with the Spekker absorptiometer for each type of powder. They are fairly low for this type of experiment, and I think quite satisfactory for a works' control method.

With regard to electron microscopy, the whole problem is one of specimen preparation; the difficulty is to get a specimen which does not show selectively one particular range of particle size. That is especially the case with particles higher than 1μ , where large particles can easily be omitted from the area examined in the microscope. Moreover, with heavy tungsten particles there is a tendency for the Formvar film to break in the electron beam. There is a good deal more work needed on the technique for examining powders. It is a very interesting field, which we should like to explore.

Mr. van Someren referred to the use of ethylene glycol. We have used it in the Spekker method, and on Type-IV tungsten it shows a larger specific surface than when using water, but there is considerable difficulty in getting rid of air bubbles and in getting the temperature down quickly if the bubbles have been removed by warming. For our purpose at least we think that the use of water is far more satisfactory. One of these higher-viscosity liquids would probably be much more useful as a research tool in powder metallurgy, where what is needed is a far more accurate determination of the particle size rather than a reproducible result which means something when it is correlated with the manufacturing process.

We are very interested in Mr. van Someren's remarks on the gain in weight on oxidation as a method of particle-size measurement. That could quite possibly be used for tungsten.

CORRESPONDENCE.

DR. F. C. ROLLASON,* M.Sc. (Member): It is interesting to note that the authors have confirmed the advantages of the rapid Spekker method similar to that described by Sharratt, van Someren, and Rollason in 1945. Sharratt † has reported comparative tests on a range of powders using the Spekker and air-permeability methods. Although the methods depend on very different physical principles there is good agreement between the surface-area figures under about 3000.

As regards deflocculants, the authors appear to have concentrated on esters and non-polar compounds, whereas our work has indicated that those substances containing highly polar groups such as (OH) or (NH₂) are most effective.

With a heavy material such as tungsten carbide, a difficulty in the Spekker determination is likely, due to settling. To minimize this difficulty the use of a very viscous liquid such as ethylene glycol, which is also an excellent deflocculant, offers some advantages but does not appear to have been tried.

DR. E. W. FELL,‡ M.Sc. (Member): I was interested in the preliminary tests carried out by the authors in their investigation of aggregation phenomena, in which tests equal weights of tungsten powder were shaken in test-tubes with various organic liquids so as to observe the resulting aggregation of the particles. The liquids were found to fall into three distinct groups in causing little, medium, and severe aggregation. It seems very probable that molecular forces associated with the liquid are the reason for this. One important measure of the inter-molecular forces in liquids is the dielectric constant, values for which are shown in Table A for each of the liquids concerned. A remarkable result is that severe aggregation is seen to occur in those liquids having the lowest dielectric constants. There would appear to be little aggregation with high values of the constant and medium aggregation with medium values, except for aniline and nitrobenzene. However, the authors imply that aniline causes more aggregation than water or alcohol (p. 58).

TABLE A.—Approximate Values of the Dielectric Constant at 20° C.

Little Aggregation	Medium Aggregation	Severe Aggregation
Water . . . 80.0	Nitrobenzene . 35.7	Ether . . . 4.33
Ethyl alcohol . 25.7	Benzaldehyde . 18.0	Petroleum spirit . 1.87
Aniline . . . 7.21	Ethyl benzoate . 6.2	Benzene . . . 2.28
	Ethyl acetate . 6.4	Paraffin . . . 1.87
	Amyl acetate . 4.88	Carbon tetrachloride 2.24
Average values 37.6	14.2	2.5

It would be unwise to infer too much from a small number of tests, hence it would be advisable to investigate the degree of aggregation in other organic liquids so as to obtain further information regarding the dielectric constant. A greater knowledge of the process of aggregation might be forthcoming by

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† *Trans. Brit. Ceram. Soc.*, 1948, **47**, 23.

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means of such correlations with the physical and chemical properties of the liquids.

I should like to thank one of my colleagues, Mr. W. R. A. D. Moore, Senior Assistant in Physical Chemistry, for helpful discussion.

Mr. A. G. METCALFE,* M.A. (Student Member): The difficulties encountered by the authors in the measurement of the grain-size of these powders are roughly the same as those which are experienced by most hard-metal manufacturers. The chief problem is that of aggregation, and the efforts that the authors have made to overcome it are very valuable.

During the treatment to produce hard-metal powders a complete range of different types of aggregation will be encountered, from the mechanically interlocked aggregate, through various stages of aggregation involving the presence of grain boundaries, to a grain formed by recrystallization and grain growth. These stages are represented by Types B to F (Fig. A) for the case of two particles, and it is assumed that mechanical interlocking (Type A) arises in the case of more than two particles.

In these representations of the section of the aggregates, the crystal orientation has been indicated by shading, and, in the case of Type B, aggregation has been shown to be aided by the surface-tension forces in a condensed phase. The stages which a powder may reach will be determined by the temperature of reduction or carburization in relation to the recrystallization temperature, so that stage F is unlikely to be arrived at in the case of tungsten powder. Even in the case of copper powder reduced at a temperature well above the recrystallization temperature there is little evidence of the aggregates being of Type F, since it has been found † that the size of the crystals determined by X-ray diffraction methods is about the same for the \pm 30 mesh powder as for — 200 mesh, suggesting that most of the aggregates are of Types C, D, E.

In the case of tungsten and tungsten carbide powders, it is evident that different size values will be obtained, depending on which particular types of aggregates are broken down in the treatment before and during measurement, and on the extent to which Type-B aggregates are re-formed. For the latter reason sedimentation methods are open to suspicion, unless suitable dispersion media can be obtained and the results extrapolated to zero concentration.

However, the object in measuring these grain-sizes is to be able to control the grain-size and size distribution in the sintered alloy. (In this connection some statistical results on nearly 150 alloys, in which the size distributions were designed to be similar, gave results confirming the conclusions of the present authors as to the existence of a relationship between the hardness of the sintered alloy and the tungsten metal grain-size, over a range around 1 μ mean size.) From this point of view, it is the ultimate particle size which is important; or, in other words, the size of the particles in the aggregates which give a single crystal of tungsten carbide in the alloy when it is sintered at a temperature below that of much grain growth. It has already been pointed out ‡ that an inherently fine-grain carbide must be used to obtain a fine-grain alloy, and this consideration is believed to involve the size distribution as well as the actual size, since broadening the size distribution appears to lead to an

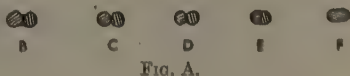


FIG. A.

* Queens' College, Cambridge.

† A. G. Metcalfe, Discussion on Symposium on Powder Metallurgy, *J. Iron Steel Inst.*, 1947, **157**, 542.

‡ E. J. Sandford and E. M. Trent, *Iron Steel Inst. Special Rep.* No. **38**, 1947, 84.

increased rate of grain growth, even at the lower temperatures of sintering. It is therefore essential to eliminate aggregation in the size measurement, because this will make the size distribution appear considerably wider than it actually is, and in some cases may give rise to a second peak in the size-distribution curve. This appears to have been the case in the paper for the powders of Types 3 and 4, where the sizes of the prepared alloy powders are coarser than those of the tungsten carbide from which they were prepared, in spite of the additional 72 hr. wet-milling, while the maximum section in the sintered alloy (Figs. 12 and 13) is well below the maximum size detected in either the prepared powder or the tungsten carbide.

The breakdown of aggregates takes place at all stages, so that finally a single-peaked distribution of sizes is usually obtained in the sintered alloy, and a method of size analysis is therefore required which will break down aggregates to this stage reached in the sintered alloy. The use of X-ray diffraction accomplishes this without actually severing the bonds between the crystals, but although the method of Stephen and Barnes * may be extended below the usual lower limit around $5\ \mu$ by the use of fine collimators, the method is not yet suitable for control purposes. It has also the disadvantage that the grain-size given is a mean.

It was found that the microscope has certain advantages over the range $0.2\text{--}5\ \mu$ for tungsten powder, because once the particles have been dispersed, the liquid used can be driven off by evaporation or allowed to set or polymerize, e.g. polystyrene or turpentine, and in this way subsequent aggregation can be avoided. If a fairly vigorous method of dispersion is used, e.g. bare glass rod on a microscope slide, breakdown of the aggregates to a stage bearing some relation to the finished powder can be obtained. Two typical determinations on the same tungsten metal powder are given in Table B. A

TABLE B.

Size, μ	Count I, Percentage by Number	Count II, Percentage by Number
up to 0.5	11.3	12.4
0.5-1.0	36.6	37.5
1.0-1.5	21.0	21.0
1.5-2.0	13.0	11.0
2.0-2.5	8.9	9.2
2.5-3.0	5.2	5.0
3.0-4.0	2.8	2.8
4.0-6.0	0.8	1.0
6.0-8.0	0.3	0.0
Total number counted	1283	523

good technique must be developed for dispersing the powder so that no separation of the sizes results, and a definite sampling method must be used. A projection microscope and mechanical counters relieve much of the strain associated with this method, so that a determination can be made in 30 min. The restriction of range to $0.2\text{--}5\ \mu$ is mainly due to the depth of focus which is available when an objective of suitably high numerical aperture is used to obtain the maximum resolution, and for this reason the method described on p. 57 would appear to be unsound.

Although it appears possible by this method to overcome the difficulty of

* R. A. Stephen and R. J. Barnes, *J. Inst. Metals*, 1937, **60**, 285.

aggregation in tungsten metal, it is restricted to a limited size range and is not so successful with tungsten carbide; this is a problem which must be solved if reliable size distributions are to be obtained, and the present authors go a long way towards achieving a solution by use of the adapted Richardson turbidimeter. The use of a simple blocking theory appears to be inadequate for sizes below $1\ \mu$ owing to the reflection from the surface of the particle, and below $0.1\ \mu$ owing to the increasing importance of wave-length sensitive scattering, obeying Rayleigh's scattering law. In many cases the two effects cancel to some extent, but from the results of Jöbst* the ratio of the apparent blocking area to the real area may be calculated. Values for totally reflecting spheres in water using green light of wave-length $0.55\ \mu$, are given in Table C, together with results for blue light of wave-length $0.4\ \mu$.

TABLE C.

Size, μ	Ratio of Apparent Blocking Area to Real Area	
	$\lambda = 0.55\ \mu$	$\lambda = 0.4\ \mu$
0.1	1.30	1.34
0.15	1.33	1.32
0.2	1.30	1.27
0.3	1.24	1.19
0.4	1.18	1.14
0.5	1.15	1.11
0.6	1.12	1.10
0.8	1.10	1.07
1.0	1.08	1.04

Some experimental results have been obtained with a turbidimetric method in conjunction with a recording microphotometer, using both constant-depth and constant-time methods. These gave fairly good agreement with results obtained by microscopic measurements and were improved by the above corrections. This work was not pursued, however, and it would be interesting to know if the authors have used any similar method of correction.

The AUTHORS (*in reply*): With reference to Dr. Rollason's remarks, it would appear that, so long as mean grain-size only is required, the optical method of determining surface area has a wide range of application. This is supported by the agreement reported by Sharratt between the air-permeability method and the Spekker method.

Our experience with deflocculants so far has not been too satisfactory: with certain tungsten powders, for instance, a given deflocculant is helpful, but with other tungsten powders the same deflocculant gives results which indicate a coarser grain-size than with water.

Dr. Rollason mentions the difficulty caused by rapid settling of the heavy powders in water and the use of ethylene glycol to overcome this. At one stage we used ethylene glycol, but found difficulty in obtaining a uniform dispersion of the powder free from air bubbles. From the one or two good suspensions made, it was clear that the dispersing properties were at least as good as water, which confirms Dr. Rollason's experience. However, except on the very coarse powders, we could not get as good a reproducibility as when using water.

A more promising approach to the problem is to mount the powder in

* G. Jöbst, *Ann. Physik*, 1925, **76**, 863.

solid Perspex. This can be done by mixing powdered Perspex with the tungsten or tungsten carbide powder and hot pressing. Bubble-free "suspensions" can be obtained and the particle size measured by light-extinction methods, and also by microscopic methods. We have unfortunately not been able to follow this up, but what little work we did showed that the amount of aggregation was not excessive.

We found Dr. Fell's contribution very interesting. From our own point of view, it is possible that Dr. Fell has given a guide which may be used in a search for more efficient deflocculating agents.

Our results are in agreement with Mr. Metcalfe's remarks on the nature of the aggregates as disclosed by X-ray diffraction methods, but we find it difficult to believe that the type-B aggregates, to which he refers, can re-form in suspension. We cannot confirm that a microscopic examination of tungsten and tungsten carbide powders, on the lines he suggests, enables one to obtain satisfactory grain-size distribution curves, as we have found that the method of slide preparation is selective, and even with the greatest care the results are open to serious error.

We did not attempt to use a corrected light-extinction equation because of lack of agreement between the different equations put forward. We were, of course, aware of the phenomenon of Rayleigh scattering and that the range of grain-sizes we investigated included some which might be small enough to involve the scattering law, but results show that for tungsten powders, using our technique with the Spekker absorptiometer, a good agreement is obtained even down to 0.2μ , as shown by the electron microscope plates.

CORRESPONDENCE ON PAPER BY DR. J. G. RIGG AND MR. E. W. SKERREY: "PRIMING PAINTS FOR LIGHT ALLOYS."

(*J. Inst. Metals*, this volume, p. 69.)

MR. L. F. LE BROcq,* B.Sc. : We are very interested in the results given in this paper, as the work described is similar in some respects to a series of tests now in progress at Farnborough. In these tests a large number of specially prepared chromate pigments of known solubilities have been incorporated in a litho oil/coumarone base. The paints so produced have been applied to chromate-treated magnesium alloy, anodized Duralumin, and phosphated mild steel, the metal specimens being finally coated with a cellulose finish. The specimens were then exposed to a sea-water spray test together with similar specimens in which neither undercoat nor finishing coat contained chromates.

So far results are only available for magnesium alloy strip (specification D.T.D. 259), but on this alloy the results are in good agreement with those obtained by the authors with potassium zinc chrome (specification D.T.D. 377A) and zinc tetroxychromate. They show in addition the superiority of D.T.D. 377A zinc chrome over D.T.D. 377 zinc chrome.

The poor results obtained by the authors with a lead pigment (red lead) are again confirmed in our work, in which three different types of lead chrome were used. This agreement is noteworthy, as it might be thought that the deleterious effect of lead would be overcome by the chromate anion.

With regard to the use of pigments not containing chromates, so far zinc oxide has been found inferior to the chromate pigments not containing lead, but lithopone is slightly superior to the best of the chromate pigments.

This result is somewhat surprising, and it is proposed to carry our experiments further with other media to see if it is generally true.

DR. F. A. FOX † (Member) : The work reported in this paper is useful in that it provides the user of painted light alloys with factual data on materials which are permissible in priming coats. Where magnesium alloys are concerned, the authors' findings are not by any means novel in so far as they apply to the use of red lead for the pigmentation of primers. It has long been known that red lead or white lead must be avoided in priming paints for magnesium alloys, and this is, for example, quite clearly stated by Beck.‡

The point that I would like to make relates to the use of iron oxide as a pigment for priming coats for magnesium alloys. Although the authors' results indicate that under their test conditions iron oxide is not harmful as a pigment for priming paints, I would suggest that it should still be regarded with reserve, at any rate where the best corrosion-resistance is required.

It is well known that local surface contamination of magnesium alloys with particles of metallic iron is very harmful to the corrosion-resistance, and

* Royal Aircraft Establishment, Farnborough.

† H. J. Enthoven and Sons Ltd., London.

‡ A. Beck, "The Technology of Magnesium and Its Alloys". 1940 : London (F. A. Hughes & Co. Ltd.).

it has further been shown * that a magnesium alloy conforming to specification D.T.D. 118 is most adversely affected in its corrosion performance if it is "protected" by a film which is rich in oxides or hydroxides of iron. In the work cited, Bushrod and I showed that magnesium-manganese sheet protected in the ordinary way with bath (iv) of specification D.T.D. 911 corroded in 3% sodium chloride solution at a mean rate of 0.24 mg./cm.²/day (total immersion time 48 hr.). The corrosion figure for the same material "protected" with a film rich in Fe(OH)₃ was 4.21 mg./cm.²/day. Thus, the presence of the iron hydroxide in the film increased corrosive attack by a factor of 20.

The conditions just quoted differed from those employed by the authors of the present paper, in that the latter have used a preliminary bath treatment conforming to specification D.T.D. 911, and this normal film is interposed between the metal itself and the iron-oxide-pigmented primer. To this extent, therefore, the present authors' conditions are safer than those of Bushrod and myself, and it is not to be expected that the use of iron oxide as a pigment will produce such a definite increase in corrosion as is represented by a factor of 20. It may even be that for many conditions the use of iron oxide would not lead to harmful results. However, should it happen that iron-oxide-pigmented primer is used on magnesium alloy parts which have been only imperfectly protected by the preliminary bath treatment, then the insulating effect of this film is partly removed, and the iron oxide can begin to come into direct contact with the metal surface; under these conditions a more or less serious deterioration in corrosion performance can be expected.

It would therefore seem to be wise to regard the use of iron oxide as permissible only where corrosive conditions are not stringent, and where the preliminary bath treatment can be relied upon to be always satisfactorily applied. If these conditions cannot be met—and particularly where high-purity magnesium alloy is being used—it would be preferable to rely on zinc chromate pigmentation.

The Authors (*in reply*): We wish to thank Mr. Le Brocq and Dr. Fox for their very interesting contributions to the discussion on our paper.

We are pleased to note the general agreement between Mr. Le Brocq's results and our own; in particular it is of considerable interest to note that there is experimental evidence for the fact that the injurious effect of lead pigments has not been successfully countered by the addition of chromate ions. The results, using lithopone pigment, are certainly unexpected, and it would be very interesting to hear in due course whether the results mentioned are confirmed by subsequent tests with other media as referred to by Mr. Le Brocq.

While agreeing in principle with Dr. Fox's remarks on the avoidance of red lead for the pigmentation of primers for use on magnesium alloys, we would add that the present work provides definite practical evidence of a marked increase in the rate of corrosion when a lead-pigmented primer is used as compared with the rate of corrosion of the unpainted light alloy, i.e. the lead-pigmented primer not only gives inefficient protection, but it is definitely deleterious to the metal; this experimental evidence does not appear to be provided by the reference made by Dr. Fox.

With reference to his remarks on the effect of iron oxide pigments, the tests described in our paper are still proceeding, and they have now reached a stage where the zinc chromate pigments are showing definite superiority over iron oxide pigments on light alloys under the more severe exposure conditions. We have not, however, so far observed any acceleration of corrosive attack (as compared with unpainted specimens under the same

* F. A. Fox and C. J. Bushrod, *J. Inst. Metals*, 1946, 72, 51.

exposure conditions) due to the iron oxide pigment used in our tests (turkey red oxide); this iron oxide pigment does not even appear to have caused any acceleration of attack, even in sea-water-spray tests, where the chromated film has been intentionally removed by scratching (Fig. 1, p. 74).

It is possible that the iron oxide or iron has to be in intimate contact with, or be an integral part of, the magnesium before it causes the accelerated attack mentioned by Dr. Fox, e.g. the iron oxide or iron must actually be part of the metal, metal surface, or chromate film. It is also possible that the method of manufacture affects the purity and composition of the iron oxide pigment and hence its corrosion protective properties.

On the basis of our continued tests it is considered that of the pigments tested, chromate pigments are preferable for the maximum protection of light alloys. Iron oxide pigment gives a reasonable degree of protection, but under severe corrosion conditions it is only recommended as an alternative when chromate pigments are not available; iron oxide pigment is certainly preferable to lead pigments for application to light alloys.

JOINT DISCUSSION ON PAPERS BY DR.
K. M. ENTWISTLE: "THE DAMPING
CAPACITY OF METALS IN TRANSVERSE
VIBRATION" AND "THE EFFECT OF
GRAIN-SIZE ON THE DAMPING CAPACITY
OF ALPHA BRASS." *

(*J. Inst. Metals*, this volume, pp. 81, 97.)

MR. M. W. THRING †: In opening the discussion on these papers I want to speak about the background of this kind of work, and how it fits in with the measurement of damping capacity and all that can be learnt from that subject in general.

I think that the work reported here is up to the usual standard of care which we expect from the Manchester school, so that I shall not attempt to criticize the experiments. The result obtained of identical damping capacity in transverse and torsional vibration is valuable, and a very nice piece of work in showing how the explanation given applies in this case.

It seems there are three aims in making damping-capacity measurements. There is first the measurement of damping capacity as a commercial test to find whether a material will be good for absorbing vibrations. That is purely an *ad hoc* procedure and the material must be tested under conditions similar to those under which it would be used. Then there is the intermediate aim, which is to determine the quality of material by damping measurements. Thirdly, there is the work particularly associated with Zener, carried out on very pure metals, where the whole aim is to find out something about the mechanism by which metals are held together. In discussing these papers all three points of view should be taken into consideration, and not only one of them.

I should like to say something about the Zener point of view, because he introduced the conception of a "relaxation spectrum". If the damping capacity is measured over a whole range of frequencies, peak damping capacities are found at various frequencies. The part of this spectrum which is involved in Dr. Entwistle's work is the extra-fast end. In the second paper, the author uses a parameter for this particular phenomenon and gets results on to one curve in a very satisfactory manner indeed. I feel that the paper should be looked at in relation to the whole story in that way, and not simply from the point of view of this particular fast relaxation, because in addition to changing the temperature, the frequency also could perhaps be changed over a wide range, for example by altering the dimensions of the specimen. In this manner quite a lot more could be learnt about the presence of peaks on the curve.

DR. R. F. HANSTOCK ‡ (Member): The first paper by Dr. Entwistle is most interesting, especially the section which deals with the effect of metallurgical conditions on the damping capacity.

* Discussion at the Annual General Meeting, London, 30 March 1949.

† Head of Physics Department, British Iron and Steel Research Association, London.

‡ Chief Physicist, High Duty Alloys Ltd., Slough, Buckinghamshire.

The phenomenon of increase in low-strain damping capacity of Hiduminium R.R. 56 during ageing at room temperature has been observed independently in the laboratories of High Duty Alloys. Employing torsional vibration, the following changes of damping capacity have been recorded in material quenched at 20° C.:

20 min. after quench : 0.005%.
 20 hr. after quench : 0.008%.
 265 hr. after quench : 0.029%.
 After ageing at 170° C. for 16 hr. : 0.003%.

These values are in quite good agreement with the author's observations for transverse vibrations.

In addition, a phenomenon similar to that described by the author for Duralumin has been observed for the alloy Hiduminium R.R. 77 (D.T.D. 683). For torsional vibration at low strains and at a frequency of 900 c./s., the damping capacity 5 min. after quenching at 20° C. is 0.007%, rising to 0.046% after 2½ hr. from quenching. Further ageing at room temperature results in a gradual fall in damping capacity to 0.017% after 167 hr. from quenching. Thermal ageing for 8 hr. at 135° C. brings the damping capacity down to 0.007%.

It is evident that phenomena of this type are not uncommon in aluminium alloys, and I should like to ask the author if he has any explanation to offer for these effects.

A relaxation mechanism may provide an explanation and it may be necessary in further work to vary, so far as possible, the frequency, and to a limited extent the temperature, at which measurements are made. R.R. 56 might be a suitable material for such experiments.

The author has shown that after ageing at room temperature for a certain time there is an increase in the damping capacity of this alloy to a quite high and possible stable value. In that state, the alloy might be very suitable for examination at different frequencies and over a limited range of temperatures.

The second paper provides notable confirmation of the validity of Zener's theory of the effect of grain-size. In this type of investigation there is one technical difficulty to which attention should be directed. The decay times corresponding to the peak damping capacities at the higher frequencies are very short. For example, the peak damping capacity observed at a frequency of 1260 c./s. corresponds to a half-amplitude decay time of just over 1 sec. Consequently the errors involved in measuring the peak values of damping capacity may be considerable if the decay times are measured with an ordinary stop-watch.

PROFESSOR F. C. THOMPSON,* D. Met., M.Sc. (Member of Council): The modern interest in the measurement of damping capacity really arose in the hope that it would enable the engineer to get over some of the difficulties associated with vibration. As methods of measurement have improved, that hope is receding. As compensation, however, it is becoming abundantly clear that both the metallographer concerned with the fundamental nature of the metallic state, and the man who is more concerned with the industrial application, are going to find in damping-capacity measurements a tool which can throw light on problems which are probably not dealt with so satisfactorily in any other way.

We already had, before this work was published, excellent means of measuring damping capacity under longitudinal stress due to Zener. The technique worked out by Frommer, Hanstock, and Murray provides adequate and satisfactory means of measuring damping capacity in torsion, but there was no

* Professor of Metallurgy, Manchester University.

really satisfactory means of doing the same sort of thing in flexure, and that is perhaps the biggest contribution which the author has made here.

I hope that a superficial reading of the first paper will not lead anyone to think that Fig. 5 represents the sort of agreement one can get in duplicate tests. The two samples *A* and *B* were not, of course, quite identical; whereas the first only received 2 hr. at the high temperature, the second had 4 hr., and I suggest that that is probably the explanation of the big quantitative difference between the two curves. Qualitatively the agreement is good.

Since we can measure all three types of vibration adequately, it now becomes possible to show that, when suitable allowances are made, the damping capacity measured by each of those three methods is identical. There was no obvious reason for doubting that previously, but it is a fact which was well worth-while establishing.

The papers also contain the first-fruits of the use of the new testing methods, and these, although only the beginning, are themselves of outstanding interest. Personally, the point which has interested me more than anything else is the really astonishing confirmation which the papers provide of the accuracy of Zener's hypotheses. If you look at the curves relating to grain-size and damping capacity, not only has the work shown that the shape of the curve is identical with that which Zener's theory predicted, but in addition, the actual position of the peak is exactly where it ought to be on the basis of that theory. I was most impressed by the agreement, and I can hardly think of any theory which has ever received more complete confirmation.

Another direction in which damping-capacity measurements are apparently going to play a very important and useful part is in the measurement of the elastic modulus. In the paper the author deals with the variation of the modulus of elasticity, and in the February *Journal* there is a very interesting paper * in which damping capacity measurements have been used as a means of determining it. In particular they seem to have extreme interest in connection with small variations of the modulus.

The author has very kindly referred to me at the end of his papers. My part was that of looking intelligent and saying "Carry on with the good work"; the rest is due to Dr. Entwistle. I should like to pay tribute to the substantial help received from the British Non-Ferrous Metals Association without which these two papers would not have been presented.

MR. L. ROTHERHAM,† M.Sc. (Member): Mr. Thring has given the background of the subject as developed by Zener, but what he omitted to do, although he did refer to it, was to give details of the different magnitudes of the effects which are due to different forms of relaxation; some of these are so high that they can be measured, if need be, with the crudest of apparatus and very reproducible results obtained.

At the Royal Aircraft Establishment we are particularly interested in the grain-boundary structure of metals, and it was that part of damping capacity which we decided to investigate; that is, the grain-boundary viscosity effects to which Mr. Thring referred. (The speaker here showed a slide to illustrate the magnitude of the effect in aluminium wire.) This kind of information is obtained from the very simplest apparatus in which a wire is gripped at two ends, supported in a furnace, and set oscillating. We have done similar work in transverse vibrations also with rather simple apparatus in which a bar is hung from a loud-speaker coil and tuned to resonance. The vibrations are picked up on a gramophone pick-up. The effects run to a magnitude of the order of 10%. I think the author's values are of the order of 0.1%; in other

* R. Cabarat, L. Guillet, and R. Le Roux, *J. Inst. Metals*, this vol., p. 391.

† Head of Metallurgy Department, Royal Aircraft Establishment, Farnborough.

words, there is a hundred times difference in the magnitude of the two quantities being observed. You could never investigate the author's kind of relaxation by apparatus of that kind.

I have been particularly encouraged in reading these papers to see the successful attempt to apply to the results the theory which has been developed in anelasticity. There are so many metallurgical problems in addition to the one being dealt with to which that theory is applicable, and I hope we shall have many more papers from Manchester University dealing with other metallurgical phenomena which, to me at any rate, are more interesting than the particular one of relaxation by microscopic thermal currents.

The first paper deals with changes in damping during ageing in aluminium alloys or copper, and I have some doubt as to whether that is the kind of problem which can be treated by the methods which have been developed. It seems to me that the theory of anelasticity is essentially a study of processes which are reversible, and I am not sure that there is any application of that kind of theory in a case, such as that of the complex copper alloys which are dealt with in the first paper, where the material is not at all the same at the end of an experiment as it was at the beginning. One of the essential requirements, I feel, is that the material should not change in this way. However, probably Dr. Entwistle had in mind not a study of precipitation as such, but more the selection of materials with low damping capacity, which showed small but interesting variations and were therefore selected as a basis for demonstrating the capabilities of the apparatus. I should like to ask the author how he proposes to apply measurements of that sort to a study of precipitation.

DR. W. HUME-ROTHERY,* F.R.S. (Member): The accuracy of Dr. Entwistle's work is becoming extremely high, and it seems to me that the stage will soon be reached at which the other factors of the problem will have to be treated with a corresponding degree of accuracy.

I would suggest that there is one slight inconsistency in the work at present and that is in the measuring of the size of crystals. The author's method is to draw a circle and magnify until it contains a specific number of grains. That is a satisfactory method and it is all one can do; but when the author comes to measure the number of twins he adopts a different procedure, and takes a straight line and counts the number of intersections which that straight line makes with twin boundaries. I would suggest that this is not consistent with the other method and that it will inevitably under-estimate the number of twin boundaries, because a straight line cannot intersect more twin boundaries than are there, although if it is nearly parallel with the boundaries it may miss some of these entirely. We have come across the same kind of trouble at Oxford, and I suggest that the only satisfactory way is to go round the crystals inside the circle and to count the number of twins.

If I might make a suggestion about this work in general, I agree with Professor Thompson that the emphasis on the work is now changing from one of engineering usefulness to one which is throwing increasing light on all sorts of metallurgical problems, and I think there is a need for a text-book on the subject. The book by Professor Zener is superb and contains a great deal, but I do not think it makes very easy reading for metallurgists. I would suggest that as the Manchester people are doing such a lot in this connection, it would be of great help to us if they would compile a text-book on this subject, written from the metallurgical point of view. Perhaps the Institute might be able to assist in this direction.

The CHAIRMAN: I am sure it will have the careful attention of the Publication Committee.

* Royal Society Warren Research Fellow, Oxford University.

PROFESSOR H. O'NEILL: It has already had the attention of the Publication Committee, and a book is being prepared.

DR. E. VOCE,* M.Sc. (Member): I should like to raise a point which is concerned more with Professor Thompson's and Dr. Hume-Rothery's remarks than directly with the papers.

Both those gentlemen inferred that there is less interest now in the engineering and practical applications of damping capacity, and I do not think that is so from the point of view of the engineer. In my work, I have constantly to answer all kinds of questions about copper alloys, and I am faced with a string of enquiries by practical people concerning damping capacity. What are the values of damping capacities for various alloys and materials? There is really very little concrete information on damping capacities of engineering alloys, information which would be very valuable if we could get it. Most of the work that has been done up to now has an important metallurgical and physical significance, but there is a real demand for the more practical type of information on the relative damping capacities.

DR. W. F. CHUBB,† B.Sc. (Member): Like Dr. Hume-Rothery, I am not particularly happy about this method of measurement or the expression of physical properties in relation to grain-size.

Some years before the war I had to study this problem, and I found that discrepancies could arise if one did not choose the right method of measuring grain-size. In particular I have noticed that throughout the whole history of this Institute—and one can go back many years—grain-size is very frequently expressed as a length, usually in millimetres, or as an area in square millimetres, and it is only on very rare occasions that one sees a grain-size reported or measured as a volume, which it certainly is. I would, therefore, suggest to the author of the present paper that his method of measurement is not strictly correct. It would be more appropriate if one were to measure and report grain-size as a volume, for obviously a grain acts and exists as a volume. Its influences are exerted as a volume in relation to other grains surrounding it, which also exist as a volume.

In measuring and examining the influences of nickel on the grain-size of copper this is very strikingly illustrated.‡ If one measures the grain-size as

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† London.

‡ *Note added in proof:* The significance of grain-size measurements on a volumetric basis are very well illustrated by reference to the influence of nickel on pure copper. As is well known, as little as 0.5% of nickel exerts a very marked effect upon the tensile, torsional, and other mechanical properties, as well as upon the density and hardness. These influences derive both directly and indirectly from the reduction in grain-size produced by the presence of nickel. Thus, measurements on a volumetric basis reveal that in the case of drawn and fully annealed materials this small percentage of nickel is effective in reducing the grain-size to one-twelfth that of the unalloyed pure metal. If, however, grain-size is expressed as the average grain width, involving measurements in one direction only across a prepared section, the observed reduction due to 0.5% of nickel is to about one-third. Clearly, only grain-size measurements on a volumetric basis are capable of providing a true indication of these influences. Such evaluations of grain-size then demand measurements of average grain width in three dimensions at right angles to one another, a procedure which necessitates the preparation of at least two micro-sections for each specimen so examined. Fuller information as to the practical applications of such measurements have been provided in "Thesis for the Doctorate", 1937 (W. F. Chubb), available in the Goldsmiths' Library, University of London, where the true significance of grain-size in relation to the corresponding influence upon the physical properties of certain copper-nickel alloys is discussed.

either a length or an area, it is not possible to correlate certain physical properties with grain-size; but if it is measured and reported as volume, then fundamental relations can be worked out much more easily.

MR. B. WALTERS,* M.A.: It seems that the disadvantage which may arise from using the intersection method of grain counting is decreased by the speed with which the grain-size measurement is made. In other words, if a calibrated graticule is put into the microscope eyepiece it is possible to move the microscope over the whole specimen and so count the number of grains over a large area. About fifty positions can be counted over the whole specimen, which largely eliminates the danger of picking one very small area and saying that it represents the grain-size of the specimen, which, of course, it does not. A large number have to be taken before a statistical picture is obtained.

DR. W. HUME-ROTHERY: I do not think you will avoid the difficulty in that way. However it is drawn, a straight line cannot intersect more twin boundaries than exist, but it can easily miss some of the boundaries which are nearly parallel to it. It follows, therefore, that a straight line will always under-estimate the number of twin boundaries.

The AUTHOR (*in reply*): It is very encouraging to find that the work which we have done has aroused so much interest.

MR. THRING made a valuable contribution in outlining the background of the relaxation-spectrum conception developed by Zener, of which this work forms only a part. As a matter of interest, one way in which it can be ascertained that variations of damping capacity during ageing arise from the relaxation phenomenon of the stress-induced preferred orientation of solute atoms is by varying the frequency at constant temperature and seeing if the peak of the damping capacity *vs.* frequency relationship occurs at a particular frequency, which might be calculated from the diffusion rates of atoms from one position to another.

It is encouraging to learn from Dr. Hanstock that he confirms the ageing results for R.R. 56 in torsional vibration. I agree with his comment that more experimental work is required in order to settle the question of the origin of that damping capacity, and I do suggest that measurement of the variation of damping capacity with frequency is the way in which to do it.

Dr. Hanstock also shot an arrow directly into the weak link of the grain-size-damping capacity curves by pointing out that the half-amplitude decay times towards the peak of the curve are quite low. The minimum value was about 1.2 sec. I agree with his statement that the measurement of damping capacity of this particular order of magnitude is not simple. The conventional methods which are used for damping-capacity measurement in the stress range are, firstly, by recording the rate of decay of free vibrations, and, secondly, by plotting the amplitude-resonance curve. The former method is ideal in cases where damping capacity is low and decay time long, and the latter method is ideal when the damping capacity is high and when the resonance curve is broad; but there is an intermediate range in which the resonance curve is too sharp and the decay time is too short to be measured accurately by either method. Measurements involving a damping capacity of 0.06% at about 2000 c./s. fall directly between those two stools. I would point out that the half-amplitude time at the peak of those curves was measured by a stopwatch, which was graduated to $\frac{1}{20}$ sec., and I submit that the error in the results was probably ± 0.1 sec. The fractional error in the value of damping capacity is approximately the same as that in the time, which probably accounts for the slight scatter which is evident at the peak of the curve.

* Imperial Smelting Corporation Ltd., Avonmouth.

Professor Thompson's suggestion that non-reproducibility of the ageing curves is due to incomplete solution is an explanation which I admit I had not thought of, and it strikes me as being plausible. Further experimental work would be required of a very refined nature in order to determine if this is in fact the case.

Mr. Rotherham's remarks concerning the ability of relatively crude apparatus to measure relaxation of a high order were very interesting. He cited a curve for grain-boundary relaxation in aluminium where a peak occurred corresponding to a damping capacity of about 18%. T.-S. Kê, who worked under Zener, developed apparatus which was capable of measuring at room temperature something of the order of 0.5%. It strikes me that the success of these experiments points to the desirability of having a sense of proportion about damping-capacity measurements. Some people are getting the impression these days that whenever damping capacity is measured apparatus loss must be of an exceptionally low order, but I submit that the work should be done to limits. One has to investigate beforehand, however, whether apparatus loss is sufficiently low and constant to justify the use of the technique.

Mr. Rotherham has developed apparatus for damping-capacity measurement, and it is interesting to know of someone actively engaged in damping-capacity work, because in my experience all too few are interested in the tremendous field of experimental research.

Mr. Rotherham suggests that at the end of ageing tests the condition of the specimen is different from that at the beginning. I submit that the changes of metallurgical condition can be followed by damping-capacity measurements without the measurements themselves affecting the metallurgical condition, which is the important factor. Damping capacity at low stress results from energy losses contributed by anelastic phenomena of some kind, which represent completely recoverable effects. The changes which take place in the specimen during ageing are by no means affected by vibration associated with damping-capacity measurements; therefore, the method is permissible.

The question of precipitation was also mentioned by Mr. Rotherham, and I would again stress that the only way in which damping-capacity measurements will be of value in this connection is in the determination of the position of solute atoms by measurement of the variation of anelastic effects of the type proposed by Zener. The question of the effect of definite massive precipitation in the material has not been investigated, but it may provide a useful field for research.

I am grateful to Dr. Hume-Rothery for pointing out the deficiency in the method of twin measurement. I was conscious at the time that there might be a more satisfactory way, but since the frequency of twinning appeared not to be significant, no efforts were made to derive a figure based on the number of twins in a given area. Subsequent speakers have stressed the importance of a sense of proportion in connection with the measurement of twin dimensions. I am also conscious of the fact that grain-size should really be determined by volume, but the method which was used is the conventional and simplest way of doing it. I might point out to Dr. Chubb that Zener measured grain-size by comparison with the A.S.T.M. standards. The image of a micro-section was projected on to a screen and then compared with these standards.

Dr. Voce raised the question of damping capacity from the engineer's point of view. It is a subject which often crops up, and I would suggest that if engineers require information on damping capacity they should carry out tests themselves, because the results which they require are unique in their application. Those which are designed for metallurgical investigations are not generally applicable to engineering conditions.

DISCUSSION ON PAPER BY MESSRS. C. BLAZEY, L. BROAD, W. S. GUMMER, AND D. B. THOMPSON: "THE FLOW OF METAL IN TUBE EXTRUSION." *

(*J. Inst. Metals*, this volume, p. 163.)

The CHAIRMAN (Mr. H. S. Tasker): I think that all members will be glad to feel that this paper is one of the first to have been awarded the Copper Pass Prize for papers of this nature. The authors received the award for 1948, and it is a happy thing that the first prize has gone to some of our members so far away.

As the authors cannot be present, I am going to ask the Secretary to read some introductory notes they have contributed to start off the discussion at this meeting.

The SECRETARY: Mr. Blazeay has asked me to read the following as introduction to this paper. He writes:

From a tube-drawing point of view, the objective in this investigation was to discover the origin of any faults that might appear from time to time in extruded shells, and, from the casting aspect, to decide on the degree of imperfection that could be permitted in the billets. With either method of approach, it was necessary to arrive at an understanding of the manner in which the metal flows under pressure in the container.

Since the paper was written, further experiments have been carried out on oxygen-bearing copper and some copper alloys.

The high-conductivity copper billets referred to in the paper were cast in two different ways, namely from an oil-fired tilting furnace and from an Ajax-Wyatt low-frequency induction furnace, in each instance with the addition of the minimum quantity of deoxidizer (lithium-calcium for the oil-fired furnace and phosphor-copper for the Ajax-Wyatt furnace) to give a reasonably sound billet as indicated by a level top. In neither instance was the content of residual deoxidizer so much as 0.01%, nor were the billets free from oxygen as judged by the hydrogen-embrittlement test. The electrical conductivity of annealed wire hot forged and cold drawn from these billets was in the region of 100% (I.E.C. standard).

To meet the objections that the oxygen content was not sufficiently high to distinguish the alloy from the straight deoxidized type, and that even a small percentage of residual deoxidizer might have affected the adhesion of the oxide scale during extrusion, several billets have since been prepared by turning down a 400-lb., horizontally-cast, tough-pitch, high-conductivity copper wire-bar to cylindrical form. In the press, these billets showed an intermediate type of flow, neither definitely of the deoxidized-copper type nor definitely of the brass type of flow. The sectioned skulls and discards gave us the impression that the tendency was for the metal to flow like deoxidized copper, but that there was a factor at work preventing the downward flow of the metal across the face of the die. If anything, the deoxidized-copper type of flow and not the brass type appeared to preponderate. The skulls in their

* Discussion at the Annual General Meeting, London, 30 March 1949.

outward appearance resembled those of high-conductivity copper referred to in the paper.

With regard to copper alloys, billets composed of 2.5% manganese, 0.02% iron, 0.02% phosphorus, remainder copper, have been found to flow like deoxidized copper. Experiments aimed at producing a non-adherent scale on 70 : 30 copper-nickel by the addition of phosphorus to the melt have so far been unsuccessful. They have shown a tendency to hot-shortness at the extrusion temperature, but whether this is due solely to the presence of phosphorus has not yet been determined. The oxide scale on the shells was not so adherent as that on 70 : 30 alloy free from phosphorus.

The 70 : 30 copper-nickel alloy used throughout was the present-day type containing up to 2.0% iron plus manganese.

We believe that useful results might be obtained by further study of the effect of various additions to copper alloys on the adhesion of the oxide scale.

Experiments have also been carried out on two grades of aluminium containing 98.8% and 99.4% aluminium, respectively. In both instances the billets flowed like brass, Figs. 4, 5, and 7 in the paper being representative of the flow in a dry or non-lubricated container, and Fig. 19 of the flow in a lubricated container (except that the billets were not of a composite nature). The pins were made of Duralumin. The billets were pre-heated to 450° C. in air in an electric furnace, and lubrication of the tools was as described in the paper for brass.

MR. C. E. PEARSON,* M.Met. (Member): This is a very welcome and practical paper, and the authors are to be congratulated on the careful and painstaking nature of the work they have done.

Extrusion, of course, has now come into its own as a primary method of fabrication which if it is not exclusive for tube, where there are rival methods, is certainly so for very many shaped products. Despite its recognized advantages, all extrusion operators will, I think, be prepared to agree that there are certain faults which can arise in extruded products, and these are clearly bound up with the flow behaviour of the metal, about which—at one time—there was considerable confusion of thought. I think we are now on much firmer ground in our understanding of the process, and I feel that the present work undoubtedly represents a further clarification of our ideas.

The fact is now familiar that in the ordinary extrusion of the brasses that are commonly extruded—the hard high-zinc brasses—the billet strongly resists movement relative to the container wall, and the surface skin tends to remain static, with the result that in the cases where one employs a close-fitting pad the outer skin is only entrained immediately in front of the advancing disc, and there gives rise to the very well known deep-seated extrusion defect. With a concentric clearance between the loose-fitting disc and the container, which is not easy to achieve, especially in horizontal presses, a complete skull can be left on the container wall which comprises the original scaled surface of the billet, and this latter method provides certainly the best means of obviating serious defects. Even so, original surface imperfections in the billet which penetrate at all deeply, can still be partly drawn in, as the authors' study of the behaviour of test skulls indicates quite clearly, and this, of course, provides a strong argument for clean well cast billets.

Some time ago I investigated a case in which extruded rods of screwing brass showed very severe blistering on their surface, with oxide and graphite inclusions just below the skin of the bar, and etched sections of the discards from this billet showed that the flow sequence was completely different from that which is usual in brass. Undoubtedly this was brought about by a

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copious and excessive use of thick graphite grease or paste applied to the press container before each extrusion; and the result of that was that the billet had moved forward bodily on the lubricated surface so that the surface had concertina-ed immediately before the die face at the opposite end to normal and was drawn in there, taking with it particles of oxide scale and graphite. This set up blistering. This represents something quite abnormal in the extrusion of brass, and it could only arise where quite excessive use of a lubricant is made.

In this sense, then, we already know that there are for direct extrusion two distinctive types of flow which we can call the unlubricated and the lubricated. Now it was found some years ago by Sachs and Eisbein that copper billets, although unlubricated in any way, tended to show this lubricated type of flow with its accompanying surface defects—blistering and so on. Their experiments were particularly marked in this respect, but they were using hexagonal-shaped billets in ordinary cylindrical containers. I am afraid most of us were inclined to attribute this peculiar flow to the hexagonal form of the billet. Crampton in America also made what we must now, I think, regard as a highly relevant observation that extruded alpha brass tended to show surface defects in contrast with the more familiar near-central defects which hard brass shows. These observations were not accorded their full weight at the time, but the present authors have shown beyond doubt that high-zinc brasses and copper billets certainly differ fundamentally in their manner of flow.

The lubricated type of flow in copper is clearly dependent in some way on the oxidized scaled surface. It would seem from the paper that this does not act as a simple lubricant: that the relevant motion is not between the scale film and the surface of the container, but that the scale actually adheres to the surface of the container and the copper slides within that. It is rather as though there were a singular lack of cohesive strength at the metal-oxide interface, thus allowing ready movement. If we could be confident that the copper scale is entirely retained on the wall of the container, then it would mean, of course, that the characteristic surface defects of this type of flow would be absent on the extruded tube. It would then appear that we could obtain under these conditions, all the advantages of the lubricated type of flow, with the absence of centralized extrusion defects, yet with none of the disadvantages of blistering which we have hitherto been led to expect.

I would like the authors' comment as to whether this is too optimistic a view; that is to say, that we could in this way obtain the advantages and none of the disadvantages of lubricated flow. If that did prove to be the case, then I think it might be possible to arrange for a suitable type of oxide film on other than copper billets to produce the same effect.

MR. W. A. BAKER,* B.Sc. (Member): I should emphasize in the first place that I do not profess to be very familiar with extrusion processes, but I read this paper with a good deal of interest because of work which some of my colleagues have been doing at the Research Association.

It seems to me that the authors' observations on the lubricating effect of copper oxide amply justify their statement at the outset of their paper that the inclusion of this paper in the large volume of literature on the subject is well worth-while.

On the whole, I thought the authors' results were presented very well in the paper; but it did occur to me, in reading it, that they might have indicated at the outset that the main object of their work was to elucidate the rather

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abnormal behaviour of copper billets. I found that I had read half of the paper before I grasped that fact.

However, the main point I wish to make is that the lubricating effect of copper oxide in the extrusion of copper which the authors describe lines up very well with work that some of my colleagues have been doing recently in the Research Association, where they have been studying the scaling of various coppers, mainly with a view to explaining the fact that some of these coppers shed their scales very easily during hot working—rolling in particular—or on cooling after annealing. Some shed these scales much more readily than others. To seek an explanation for this behaviour, they have studied the mechanical properties of the scales at elevated temperatures, and found that in many cases the scales formed have an astonishing capacity for deformation, even in tension. In other cases the scales are much less plastic, and I think on the whole the different scaling behaviours are quite well explained in terms of the mechanical properties of the bulk scales. The coppers which the authors have used form scales of a kind which would be plastic under the conditions which obtain near the walls of the extrusion container, and it seems to me that their observations on the lubricating effect of the copper oxide scale tie up very well with my colleagues' observations.

There is one minor point on which I am not quite in agreement with the authors. Mr. Pearson referred to it a few minutes ago. The authors suggest that the copper billet actually slides inside the oxide coating. I wonder whether it is necessary to make that assumption. As I have said, the bulk scale is plastic and in the extrusion of these copper alloys there is a very substantial temperature gradient in this scale, so that the scale which is in contact with the container wall must be a good deal colder than the scale in contact with the metal, the metal being of high conductivity and the scale of relatively low conductivity. It is quite reasonable to suppose that the most plastic part of the scale is that part of it which adjoins the copper billet, and most of the plastic deformation of the scale will occur in this part. Therefore it does not seem necessary to assume that there is something curious about the bond at the junction of the metal and scale, as the authors' statement implies.

DR. R. GENDERS,* M.B.E. (Member): I found this paper extremely interesting. It deals with experimental questions which are very difficult to determine, and the authors are to be very highly congratulated on a mass of painstaking and careful work. As far as I know, this is the first research paper to be published on the factors of tube extrusion, and it has several novel aspects, particularly the method of examining the thin shell left in the container to provide indications of the flow which has occurred in the billet.

The relation of these results to the production, in practice, of defects in tubes seems to have confirmed the results broadly, and the work is thus of considerable value from a practical point of view.

The extrusion of tubes is rather different from the extrusion of solid rods because in the extrusion of tubes the mandrel is present, but it moves so slowly that it can be considered as virtually fixed parallel to the outside wall of the container. Thus, in considering the axial section of the billet we can ignore one half and consider tube extrusion as being fundamentally the extrusion of a billet through a die aperture near its periphery. I have taken that view in some experimental work I am doing on the extrusion of thin plates of translucent wax in which the flow can be observed during the pressure stroke. The case of tubes is dealt with by extruding the plate through a slot at one edge. The indications are broadly such as have been shown by the

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authors, but it is clear that much work is needed on this question before we can draw definite conclusions.

The main point of the paper is that the type of flow in extrusion of tubes is influenced to a marked extent by the presence of lubricant between the billet and the container, and there, I think, we are quite agreed. There is plenty of evidence of it. But it is postulated by the authors that copper oxide is endowed with rather high lubricating properties, and some of the results are somewhat puzzling and not altogether consistent with that view. When one considers that copper oxide, as far as we know, is not a plate-like crystalline structure, such as molybdenum sulphide and graphite, then I think we are justified in asking the authors if it is not possible to present a little more evidence. Mr. Baker has added some very interesting information, but I do not think it is sufficient to be really conclusive.

Now, in searching for other possible explanations of the difference in flow between copper and brass, it has seemed to me that the temperature gradient in the billet might be quite important. Obviously in copper, which is a very highly conductive material, there is practically no temperature gradient between the inside and the outside of the billet, whereas in brass there is a very steep temperature gradient. The outside of the billet, owing to the cooling effect of the container, is very much cooler than the inside. Consequently, with a copper billet there is a relatively hotter skin region which is more able to flow, and this apparently dictates the type of flow characteristic of copper and other conductive metals.

In this connection, however, the properties of copper oxide as an insulator may be quite important, so that we need not, I think, stick to the idea of copper oxide being solely a lubricant. This question needs a good deal more investigation, and I hope very much that the authors will continue their very excellent work.

MR. BAKER: Arising from Dr. Genders's contribution, I hardly think all the difference between the behaviours of the copper billets and brass billets could be explained in terms of the temperature gradient through the metal. Do not the authors show that a brass billet with a thin copper sleeve behaved just as a copper billet did?

DR. GENDERS: Not a thin one; that does not work.

MR. BAKER: I understood that they plated it.

DR. GENDERS: Thickly.

MR. BAKER: I suggest that as we are talking about a billet 6 in. in diameter, the distinction between a thick and thin sleeve, when we are discussing the mode of flow of the billet, is something quite substantial. From the authors' observations on the brass billets we have to account for a stiff region of the order of $\frac{1}{2}$ in. or more thick. Even a thick copper plate could hardly affect the temperature gradient in the brass at a depth of $\frac{1}{2}$ in. or more.

DR. GENDERS: I do not offer an explanation. All I suggest is that the authors should take into account other possible operative factors in order to complete the explanation themselves.

MR. C. E. PEARSON: There is one other answer to the question, and that is that aluminium and aluminium alloys are extruded usually from heated containers which are practically at the temperature of the billet. Aluminium

alloys are also good conductors, and they certainly give a non-lubricated type of flow as far as I know.

CORRESPONDENCE.

DR. D. K. CRAMPTON,* M.S. (Member): The authors have shown great ingenuity and technical skill in carrying out the present investigation. Their interpretations of results seem rational throughout.

In our plants we have not made investigations of the type here described, but our general background of experience confirms their conclusions. It has been realized that a relatively greater diagonal flow occurs as the ratio of billet-container frictional shear stress to internal billet shear stress increases, whereas relatively greater axial flow occurs as this ratio decreases. The work here reported gives a much more precise picture of the flow paths than has been available before. The importance of the oxide coat on copper in determining its flow in an unlubricated container has been recognized, but there has been some speculation as to whether its function was to permit slip between the billet as a whole and the container or between the billet proper and its oxidized surface. Have the authors given consideration to the former possibility?

Some years ago it was our practice to use a lubricated container for extruding brasses, and occasional difficulty with blisters was encountered. The incidence of such blisters when extruding aluminium brass was very much greater than with the other brass alloys. The conclusion was finally reached that the lubrication of the container was responsible and thereafter this lubrication was discontinued although the mechanism of formation of the blisters was not fully understood. The explanation by the authors seems adequate although it still does not completely explain the difference between aluminium brass and other brasses as stated above.

It would be interesting to know whether the authors have made measurements on the relative amounts of extruded tube which would have to be scrapped for external defects when using a lubricated container and for internal defects when using an unlubricated one. In the latter instance it would be assumed that resort would be made to expanding of samples on a tapered pin or other test for quality of the back end of the extruded tube.

The question is raised as to whether they have observed any effect of the different types of flow on the concentricity of the extruded tubes produced. Finally, have they used their method to study the effect of shape of die and dummy block on flow pattern?

The AUTHORS (*in reply to the discussion and correspondence*): We deeply appreciate the distinction of having been among the first to receive a Capper Pass Award, and we take this opportunity of publicly thanking the donors, Messrs. Capper Pass and Son Ltd., of Bristol, for their generosity and encouragement.

The discussion on the paper centres mainly around the manner in which copper flows within its oxide envelope, but although this was an interesting part of the investigation it was scarcely more important to us than the flow of brass and other alloys.

Mr. Pearson's suggestion that there may be a possibility of alloying "other than copper billets" so as to produce a plastic scale like that on deoxidized copper may, to use his own word, be "optimistic" for some alloys, but it is

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within the bounds of practicability for others. We had that end in view when we added phosphorus to 70 : 30 copper nickel, an alloy which forms a thick, adherent scale when heated in an oxidizing atmosphere and one which adheres to the outer surface of the skull in the container. The idea could be extended to the brasses containing more than about 86% copper in which copper oxide preponderates in the scale, but in the commoner types of extrusion brasses containing 60-80% copper the preponderance of zinc oxide in the thin scale appears to be a handicap, unless an ingenious person can think of a way of improving the plastic properties of zinc oxide.

Perhaps it may be within the scope of the discussion to refer to our experience during the war when we were unable to obtain O.F.H.C. copper and were forced to find a substitute for uses requiring the sealing of copper rod and tubing into glass. As is well known, a high-conductivity copper free from susceptibility to hydrogen embrittlement and having an adherent oxide scale is necessary for this sealing work. We found that copper deoxidized with 0.05% manganese was a fairly satisfactory substitute. The scale was adherent at high and room temperatures in ordinary heating and quenching tests, yet recent experiments on the extrusion of copper billets containing 2.5% manganese with some iron and phosphorus, mentioned in our introductory remarks to the discussion, showed that the billets flowed like deoxidized copper. We have not pursued this matter further, but there is a probability that iron and phosphorus, both of which help to form a flaking scale, counteract the effect of the manganese.

The copper type of flow is, of course, only desirable if the oxide envelope is left in the container and the surface of the billet is free from defects. If an appreciable proportion of the oxide passes down the die with the billet it might be difficult to remove by subsequent pickling, while if there are defects on the surface of the billet they could quite easily affect the quality of the shell. We have found, for instance, that fine black streaks on the outer surface of copper tubes, appearing as early in drawing as the first pass, originate in depressions on the surface of the billets which become coated with oxide during pre-heating. These streaks invariably open out when filed.

We are pleased to hear from Mr. Baker of the work being carried out by the British Non-Ferrous Metals Research Association on copper scales, for we believe that the solution to some extrusion problems can probably best be found through a study of small pieces of metal oxidized and deformed under controlled laboratory conditions.

The point raised by both Messrs. Pearson and Baker that we have not proved that copper slips, as it were, at the metal oxide interface could be investigated in the following way: If, as they suggest may be the case, slipping occurs within the oxide itself, then some oxide should be carried down the container and across the face of the die on to the outside of the shell. Whether or not this is so would appear to depend on the possibility of identifying the oxide on the extruded shell as having come from the oxide envelope in the container or, alternatively, as having formed on the hot shell immediately after extrusion. We do not wish, however, to press the suggestion that copper slides from its oxide envelope at the metal-oxide interface. The line of slip could at least be expected close to that interface as the oxide would probably be in its most plastic state at that position.

Characteristic features of a copper skull are freedom from oxide and a smoothly scored outer surface on which the score lines are often in relief and likely to disappear part of the way down the skull. Although some of these features give one the impression that the skull has slid under pressure past the oxide envelope in the container, they have to be considered in the light of strong evidence that a copper skull is formed by a kind of back-extrusion of the top outer portion of the billet (Fig. 18 in the paper), and not by the action

of the disc in cutting through the outer layer of billet, as with brass. The evidence points to the probability that the outer surface of the skull is an impression of the inner surface of the oxide envelope after billet and envelope have parted company. A little more thought on this aspect of the problem may reveal a means of proving whether slipping occurs within the envelope or at the metal-oxide interface.

Dr. Genders raises the question as to whether the oxide on a copper billet functions as the equivalent of a lubricant or as an insulator. If it acts as an insulator then one would expect that if an insulating layer could be placed on a brass billet the brass should exhibit the copper type of flow, while if a copper billet could be inserted in the container completely free from oxide it should exhibit the brass type of flow. There are experimental difficulties in testing these deductions, but we shall give them some thought. We are, however, inclined to agree with what we assume to be the views of Messrs. Pearson and Baker that plasticity rather than insulating properties in the oxide determines the mode of flow.

Another point is this: If insulating properties are of prime importance then how can we explain the difference in type of flow with brass when extruded first in a dry container and then in one having a thin layer of grease. Have we to suppose that the grease is an insulator?

The fact that cuprous oxide has a crystal grain somewhat like that of copper and is not a plate-like substance like graphite should not be of much consequence, as high-temperature plasticity is involved in the supposed slipping.

Dr. Crampton mentions still another possibility with the oxide, namely that it might permit slip between the billet as a whole and the container wall. The facts that oxide accumulates on the wall and that the skull emerges from the press free from oxide seem to indicate that the oxide does not "lubricate" the container so much as function as a "lubricant" for the billet within the oxide.

We agree with Dr. Crampton that some blistering on aluminium-brass shells is difficult to explain. Blistering due to the metal cutting across the dead corners of the billet is usually easy to distinguish, but the origin of some blisters is obscure. We feel sure, however, that blisters on the first part of the shell to be extruded are often due to axial porosity in the billet. When this porosity extends laterally beyond the diameter of the mandrel it is bound to pass into the shell and be revealed as scale and blistering on both inner and outer walls. We refer not to simple piping but to intercrystalline shrinkage obscured by the saw-cut when the as-cast billet is sawn—into extrusion lengths.

With regard to the relative quantities of scrap made by the lubricated and unlubricated methods of extrusion, we cannot supply data that are of much value for works' guidance as we have avoided large-scale production from lubricated containers. We understand that some firms make a practice of lubricating the container of vertical presses similar to those described in our paper and, moreover, that they extrude without cutting a skull, but up to the present we have not succeeded in using a lubricated container on a production scale without a danger of blistering. In our experiments with greased containers we have had to reject the greater portion of the shell for external blistering, and when using a greased disc we have had to reject about 18 in. of the last portion of the shell on 80% of shells.

With regard to concentricity, we have no evidence that it has anything to do with the type of flow.

Lastly, with regard to shape of dies and discs, we have not so far attempted to alter the angle of the die, but we intend to do so. Some experiments have been made with discs of different shape in our study of internal blistering. Two types were used: (a) one with parallel upper and lower surfaces normal

to the vertical, and (b) one with the lower surface at the usual angle of 130° but with three concentric steps or re-entrant angles. So long as lubricant was applied to the under-surface of the disc, blistering appeared on the inner wall of the shell irrespective of the shape of the disc, although to a lesser degree with (b) than with (a). A serious disadvantage with (b) is that the discard adheres tightly to the steps or grooves.

DISCUSSION ON PAPER BY MAJOR P. C. VARLEY: "THE RECOVERY AND RECRYSTALLIZATION OF ROLLED ALUMINIUM OF COMMERCIAL PURITY." *

(*J. Inst. Metals*, this volume, p. 185.)

DR. T. LL. RICHARDS,† B.Sc., F.I.M. (Member): As is most fitting, recovery and recrystallization are receiving much attention by research workers in America, Britain, and France at the present time. The study of these processes is essential, not only to gain an insight into their fundamental nature but also so that metals may be handled intelligently and used to the fullest advantage.

Although there are many points raised in the present interesting and valuable paper which are worthy of the fullest discussion, I think that we should be wise to restrict our attention to the main objective of the investigation, which is, as stated on p. 186, to determine whether recovery and recrystallization are two distinct processes or merely two stages of a single process. There are some, like "Skimmer" of *Metal Industry*,‡ who have passed judgment already, and who believe that the author has established by his observations that the two processes are merely two stages of a single process. I think that on this occasion "Skimmer" has jumped "Out of the Melting Pot" into the fire.

Major Varley himself is a little more cautious, and is not prepared to go quite so far. He considers (p. 201) that since the activation energy of the softening process is sensibly the same whether it is measured at the recovery stage or after the onset of recrystallization, then the two processes are similar in their nature. This kind of argument is not altogether satisfactory; it is almost equivalent to saying that two articles bought at a shop for the same price are similar. In fact, it is the similarity in activation-energy values that makes a distinction between recovery and recrystallization difficult. In certain instances, as Dr. Cook and I have shown for an aluminium-copper-magnesium alloy, by structural observations and in ordinary annealing curves, the two processes are quite distinct,§ while with cold-rolled copper || the same conclusion is reached only by analysis of isothermal annealing rates.

The author claims that his isothermal curves exhibit no discontinuity, but I think it would be fair to say that the only complete curve in Fig. 2 of the paper shows a distinct change of direction at a point corresponding to a tensile strength of $7\frac{1}{2}$ tons/in.² Since the first sign of recrystallization was observed when the aluminium sample had decreased in strength to this value on isothermal annealing, then the initial decrease must have occurred by another process. Not only does the curve show two distinct sections, which I think are evidence of two distinct processes—recovery and recrystallization—

* Discussion at the Annual General Meeting, London, 1 April 1949.

† Research Department, Imperial Chemical Industries Ltd., Metals Division, Birmingham.

‡ *Metal Ind.*, 1949, **74**, (8), 142.

§ *J. Inst. Metals*, 1948, **74**, 583.

|| M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1947, **73**, 1.

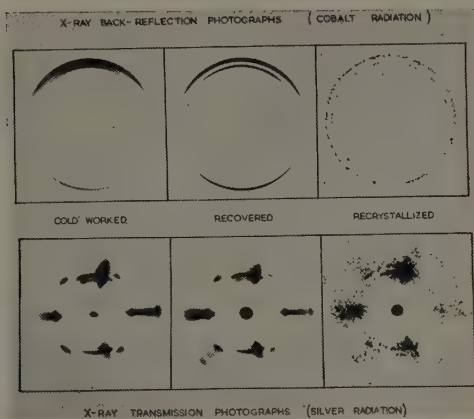


FIG. A.

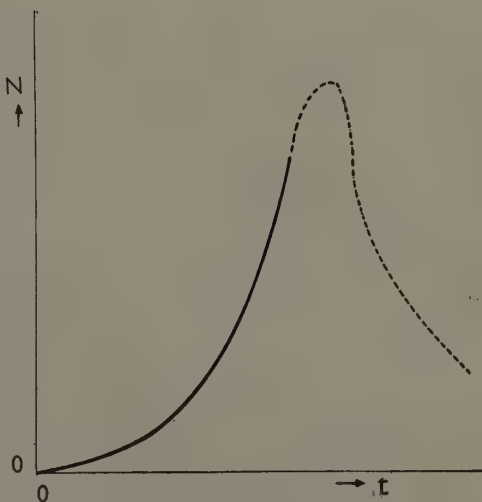


FIG. B.—Progress of Nucleation.

[To face p. 1034.

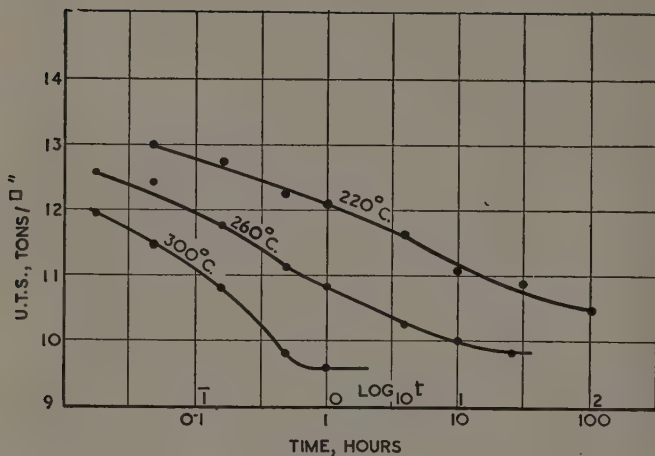


FIG. C.—Isothermal Annealing Curves for Aluminium-2% Magnesium Alloy.

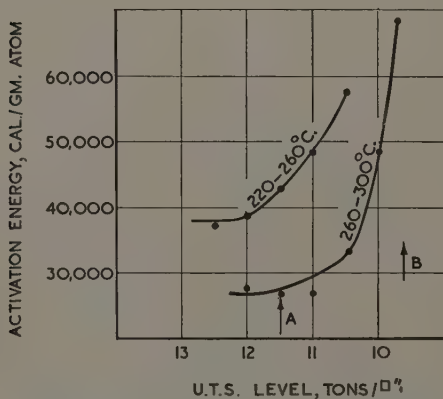


FIG. D.—Variation of Activation Energy with Temperature and Degree of Recrystallization in Aluminium-2% Magnesium Alloy.

A = Beginning of recrystallization.

B = End of recrystallization.

but the author would have observed two structural changes had he used the X-ray back-reflection rather than the transmission method.

This point is illustrated in Fig. A (Plate CXXIV), which was prepared by my colleagues Dr. G. Parker and Mr. S. F. Pugh, and is a composite reproduction of X-ray back-reflection and transmission photographs of commercial aluminium cold rolled 95%: as rolled, after annealing for 16 hr. at 200° C., and after $\frac{1}{2}$ hr. at 500° C. There is no change in the character of the transmission photograph after the first annealing treatment, even though there was an appreciable change in D.P. hardness. There is, on the other hand, marked improvement in the definition of the high-order diffraction rings in the back-reflection photographs, indicating removal of lattice distortion or recovery.

The corresponding transmission photograph shows that recovery has occurred without significant change in crystal orientation, since the pattern is identical with that of the material in the as-rolled condition. The structural changes associated with recovery must be short-range in character and may involve removal of lattice distortion by a process of dissolution of dislocations, as the author suggests. Lacombe and Guinier,* the former by a metallographic technique and the latter by a sensitive X-ray technique, have now established that recovery occurs in aluminium and aluminium alloys by the formation of strain-free mosaic blocks within the initial distorted grains, the mosaics within individual crystals being very slightly disoriented with respect to each other. Both transmission and back-reflection photographs of the sample annealed at 500° C., however, show that recrystallization has occurred with the generation of new crystals and with some re-orientation of the structure. While recovery may be a process of dissolution of dislocations with removal of lattice distortion, it would seem that recrystallization involves more general atomic re-arrangement. I think that this effect ought to be associated with the polygonization phenomenon which has been observed by Cambridge workers and reported by Cahn;† that is, recovery, the development of mosaics, and polygonization should all be regarded as one and the same thing.

In my own view the evidence is overwhelmingly in favour of the conception of recovery and recrystallization as separate processes, but I should welcome a full and dispassionate discussion of the question.

MR. R. J. L. EBORALL,‡ M.A. (Student Member): I was very glad to see a paper on this subject including "recovery" in its title, since there is not very much information on recovery. I should like to congratulate the author on what is, I think, a very nice piece of work. I hope that in view of the date (April 1) I may also be permitted to speculate a little and to disagree to some extent with Dr. Richards.

Broadly speaking, the study of recrystallization and related subjects can be divided into work on kinetics and work on structural changes. On the kinetic side, one of the most surprising developments is the result obtained by Mehl and his collaborators when they measured the rates of nucleation of new crystals and the rates of growth of new crystals, and found for the rates of nucleation of new crystals curves of the type shown in Fig. B (Plate CXXIV), where the number of nuclei N formed per unit time in the unrecrystallized matrix is plotted against time t . Nothing much happens for a long period, and then the rate of nucleation goes up very markedly. In certain conditions it may reach a maximum and then go down again, as shown by the dotted line.

* *Métaux et Corrosion*, 1948, 23, 212.

† R. W. Cahn, *Phys. Soc.: Rep. Conf. on Strength of Solids*, 1948, 136.

‡ Head of General Metallurgical Section, British Non-Ferrous Metals Research Association, London.

A further observation on much the same lines was made by Dr. Cook and Dr. Richards,* who found that the actual recrystallization in copper was delayed, and postulated a two-stage mechanism by which recovery was necessary to recrystallization. There again there is a delay before recrystallization sets in. The present author has again shown this kind of effect, where recrystallization sets in only after the tensile strength of the metal has fallen to a certain value and after quite a long incubation period.

With regard to the type of curve found by Mehl and his collaborators, Turnbull has recently published a paper † in which he gives an account of the nucleation processes as modified by the necessity for diffusion. He bases his theory on the work of Volmer and of Becker, and modifies the results to take into account the diffusion time for atoms to migrate through the lattice and collect to form the nucleus, and obtains curves of this type. Obviously that kind of consideration is valid if the formation of a nucleus involves a change in the local concentration of some component, as it does for many phase changes, but it does not seem to me that it can be valid in a case such as this, where the atoms which are to take part in the process are already on the spot.

I should like now to say a few words about what happens in recovery. Dr. Richards has mentioned the relief of micro-stresses, or at least the line-sharpening effect in back-reflection photographs, and it is generally agreed that line broadening in the first place is due to small-scale stresses. He has also mentioned the work of Guinier and Lacombe and of Cahn in showing the fragmentation or polygonization of crystals during recovery. This fragmentation process is also being studied in our laboratories by Miss Silcock, using a different X-ray technique which gives the same kind of result.

I think that where I would differ from Dr. Richards is this. He says that these processes are something quite distinct from recrystallization; I think, on the other hand, that it may well prove that these processes are the whole key to this difficult feature of the delay in the formation of the nuclei on which recrystallization proceeds.

Returning to the results of Miss Silcock in our laboratories, she finds that the first of these recovery processes which becomes apparent in certain alloys is the removal of the line broadening. After that the fragmentation process proceeds, and the crystals, which were originally bent or distorted so that the reflections were continuous over a certain angle in her technique, change progressively so that maxima develop in the reflections, and these eventually become more or less distinct spots, covering the same angular range as the original reflection.

As regards fragmentation, that is much the same result as was obtained by Guinier and his collaborators, though possibly slightly different in the progress of the reaction. The point that I want to make about it, however, is that different parts of the crystal and different parts of different crystals change at somewhat different rates, and consequently in certain regions more or less perfect fragments may very likely be formed before they are formed in other regions. I think that it may well prove that the first fragments to become perfect in a crystal are in fact the nuclei on which recrystallization proceeds.‡ That is perhaps pure speculation, but we hope to be able to carry out some experiments directed towards testing that idea. Whatever the true state of affairs is, however, and whatever the theory which is ultimately put forward, Major Varley's measurements on activation energies will be most valuable for testing it.

* *loc. cit.*

† D. Turnbull, *Metals Technol.*, 1948, 15, (4); *A.I.M.M.E. Tech. Publ. No.* 2365.

‡ This view is largely due to Cahn (private communication, June 1948).

The AUTHOR (*in reply*): I should like to thank Dr. Richards and Mr. Eborall for their very interesting contributions to the discussion. I am inclined to agree with both of them, which is perhaps a little difficult because they seem to disagree amongst themselves; but it is going to be a matter of extraordinary difficulty to sort out whether recovery and recrystallization are, in fact, two different things or whether they are merely the same process going on continuously. I think that a solution will be achieved only by the joint efforts of workers all over this country and the Continent and America, tackling the problem from various points of view. Every little bit of evidence put forward on the subject throws new light on the process, and it is only by a process of gradual approach such as that, that we are likely to reach the truth.

I may say that since the work described in this paper was concluded I have been doing some further work, this time on the alloys of aluminium with various other elements, and I propose to illustrate results on alloys of aluminium with magnesium. Fig. C (Plate CXXV) shows some isothermal annealing curves obtained with an alloy of aluminium with 2% magnesium. There is nothing else present; the aluminium used was super-purity. It will be seen that the curves are somewhat similar to those obtained with commercial-purity aluminium, but they differ in two important respects. In the first place, they differ in shape according to the temperature at which the annealing is carried out. They become flatter and flatter as the temperature drops, so that they are no longer superposable by displacement along the time axis. The second respect in which they differ is that they are more widely spaced with temperature as the temperature falls.

I think that both those points are perhaps more clearly illustrated in Fig. D (Plate CXXV), where the calculated activation energy is plotted against the ultimate tensile stress. With commercial-purity aluminium the activation energy seems constant at just over 50,000 cal., irrespective of the tensile-strength level at which it is determined, and it does not change on passing over from recovery to recrystallization. The situation is very different with the magnesium alloy. Apparently—I say “apparently” because experimental difficulties make it difficult to determine points any further to the left—the constant activation energy in the recovery period is very much lower than for commercial-purity aluminium, and on passing over from recovery to recrystallization the activation energy rises steeply right through until recrystallization is complete. You cannot determine it any further to the right, because the process is finished.

The other point is that, as I have said, the values of the activation energy are very different according to the temperature range over which they are determined. That, I think, must be due to the fact that one is really dealing at the two temperatures with two different alloys; probably different amounts of magnesium are in solid solution.

It would be very nice if points could be determined towards the top of the curve, but the difficulty is one of time. It is very difficult to find any means of heating up a piece of metal to the temperature required quickly enough for the time of heating to be small compared with the annealing time, when the latter is of the order of 1 sec. If I could heat a piece of aluminium to a steady temperature in 0.1 sec. and leave it there, I should be very happy.

This further work suggests to me, at any rate, that the identity of the activation energy for recovery and recrystallization for commercial-purity aluminium is more in the nature of a coincidence than anything else. Here one has the addition of 2% magnesium to aluminium producing an entirely different state of affairs, where a very different activation energy for recovery is found, increasing rapidly on passing over to recrystallization.

Incidentally, the activation energy of full recrystallization seems to be

considerably higher than that for pure aluminium, while the activation energy of recovery is considerably lower. I do not pretend to understand that at the moment. That state of affairs seems to hold for magnesium-containing alloys, but entirely different results are obtained if instead of the magnesium manganese, for example, is added; it appears to act in almost exactly the opposite way.

CORRESPONDENCE.

DR. N. THORLEY *: This paper is to be welcomed because it re-emphasizes the vagueness which is current in the meaning and interpretation of the terms "recovery" and "recrystallization". There is an obvious need for more stringent definitions of these processes, a statement of the exact conditions for which these definitions obtain, and a discussion of their mechanism in relation to annealing schedules, with the accompanying changes in mechanical and other physical properties. The theoretical side of the subject is also far from satisfactory, and until this can be developed further it is to be hoped that more experiments of this type will be carried out.

The onset of recrystallization is usually observed microscopically or by the appearance of individual spots on an X-ray photograph. Since it is quite possible that the first recrystallization nuclei are deposited at zero time, or at any rate, very soon after, these methods do not reveal the true onset of recrystallization, i.e. when the crystallites are of the order of 10^{-5} cm. Certainly the appearance of X-ray spots, the criterion used by Varley, gives only the time at which the new, soft crystallites have grown to about 10^{-3} cm., which cannot therefore be the true onset of recrystallization. This coincides with a tensile strength of $7\frac{1}{2}$ tons/in²., but actually recrystallization has been proceeding for at least part of the time the strength has been falling to this figure. No discontinuity is therefore to be expected at this point in the annealing curves, since it is only an arbitrary boundary set by the method of observation used. Further, it is unlikely that a discontinuity would separate the recovery from the recrystallization part of the process, since it is not impossible that both may begin at zero time and continue simultaneously throughout the anneal. In Varley's experiments, using aluminium with 75% reduction at temperatures above 200° C., the so-called recovery process, corresponding to the initial release of internal strain, has probably been completed within the first few seconds of the anneal, before the first U.T.S. measurement was taken, even at the lowest temperatures used. There is no real evidence of the $7\frac{1}{2}$ tons/in.² figure separating recovery from recrystallization, and hence no change in structure is observed. In fact, Varley's experiments may follow recrystallization *only*, and the constant slope of all his $\log t - \frac{1}{T}$ curves, for different conditions of specimen, lends support to this idea.

As Varley points out, recovery and recrystallization must take place at any temperature, but they may also be taking place simultaneously at any time. It is true that they are probably very similar in their nature, but this cannot readily be deduced from isothermal annealing curves.

The absence of an incubation period in these experiments is in keeping with Anderson and Mehl's observation that no incubation period is found for aluminium of similar purity with 90% reduction at 325° C.

It seems necessary to devise some experiment to measure recovery and recrystallization separately, if their difference is physically significant and if

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they are separate in time, before any precise definitions or formulations of these expressions can be made. Only then will it be possible to test the relative merits of the rival one-stage or two-stage process theories over which there is so much controversy. At present, annealing experiments cannot give any positive evidence of the movement of atomic dislocations, so that it seems better to give the results of experiments only.

The most direct line of approach to the problem is a wider application of the X-ray method. A fundamental investigation is needed to correlate any changes of crystallite size, lattice distortion, preferred orientation, and lattice parameters with temperature and time of anneal. All these changes could be followed by a full use of the X-ray technique, and already there is some evidence of success in identifying the recovery period.* It may be necessary to use the micro-beam method to study individual crystallites.

When this stage has been completed, these changes could be correlated with the corresponding changes in mechanical properties and those physical properties which respond to the annealing treatment. Quenching methods should be avoided wherever possible unless it is absolutely certain that quenching strains are not introduced, or that the properties being studied are not affected by them. It should be possible to measure many of these properties *during* the anneal and not on a specimen quenched from the annealing temperature.

It is hoped to make further discussion of these problems the subject of a later contribution.

The AUTHOR (*in reply*): I should like to thank those who have contributed to this interesting discussion which has, I think, helped to throw some light upon an interesting problem. It is, of course, true, as Dr. Thorley suggests, that the X-ray method used cannot detect the true onset of recrystallization but only the time at which the new crystals have grown to a given size. The same is, of course, true of any other method though the limiting size may be different. I suggest that the curves reproduced as Figs. C and D show that this limitation is not a serious one and that the initial portions of the U.T.S. curves are related to recovery only.

Dr. Thorley compares my experiments with those of Anderson and Mehl and suggests that the absence of an incubation period is in accord with their observations on aluminium with 90% reduction. I do not think this is a fair comparison, as Anderson and Mehl were observing the first appearance of new crystals under the microscope, corresponding to the drop in U.T.S. to $7\frac{1}{2}$ tons/in.² Thus, translated into the terms of Anderson and Mehl, all my curves show an incubation period, but at 325° C. this would be of the order of 1 min., which would not be apparent on the curve given by them.

I think Dr. Thorley puts his finger on the vital spot when he calls attention to the necessity of devising some method of measuring recovery and recrystallization separately over the whole range of the softening process. This certainly cannot be done by the method I have described, and it is to be hoped that development of X-ray methods such as described by Mr. Eborall will facilitate it.

* H. D. Megaw and A. R. Stokes, *J. Inst. Metals*, 1945, **71**, 279.

JOINT DISCUSSION ON PAPERS BY MR. W. I. PUMPHREY AND DR. P. H. JENNINGS: "HIGH-TEMPERATURE TENSILE PROPERTIES OF CAST ALUMINIUM-SILICON ALLOYS AND THEIR CONSTITUTIONAL SIGNIFICANCE" AND "A CONSIDERATION OF THE NATURE OF BRITTLINESS AT TEMPERATURES ABOVE THE SOLIDUS IN CASTINGS AND WELDS IN ALUMINIUM ALLOYS"; AND ON PAPER BY MR. W. I. PUMPHREY AND MR. D. C. MOORE: "A CONSIDERATION OF THE NATURE OF BRITTLINESS AT TEMPERATURES BELOW THE SOLIDUS IN CASTINGS AND WELDS IN ALUMINIUM ALLOYS." *

(*J. Inst. Metals*, this volume, pp. 203, 235, 257.)

MR. W. I. PUMPHREY introduced the three papers and added that experiments carried out subsequently to their publication showed that increase in speed of welding, rate of cooling, or degree of restraint increased the tendency for weld cracking to occur.

DR. E. G. WEST,† B.Sc. (Member): I have had the honour of opening the discussion on several previous occasions on other contributions by the various members of the A.D.A. welding research team at Birmingham, and I assume that the only reason why I have been asked to open the discussion again is to emphasize that the work is continuing along the lines previously described. It is considered that by an investigation of the fundamental metallurgical factors involved in melting and solidification it should be possible to improve the weldability of several of the groups of aluminium alloys. By "weldability" is meant not only the ease with which a weld can be made but also the qualities of the resulting complex.

Previous papers have dealt almost entirely with fundamental metallurgical characteristics of alloys under equilibrium conditions. I believe that the present papers indicate that the basic work and results published hitherto are in general applicable to alloys under non-equilibrium conditions—that is, the conditions in which the materials are normally welded or cast—and, while these papers do not indicate that we are at the stage where alloys can be "tailor-made" to give good welding properties coupled with other satisfactory properties, many of the fundamental requirements have been set out,

* Discussion at the Annual General Meeting, London, 1 April 1949.

† Technical Director, The Aluminium Development Association, London.

tested, and in my opinion, proved, by the various experimental methods described. Incidentally, the experimental techniques previously used by these investigators continue to delight all those who are interested in careful experimental work of the very high order of accuracy shown here.

Another aspect of the work deserves emphasis, namely, that these results now require to be applied by the industries concerned with the materials—partly by the producers of the alloys and partly by the users who require to weld them. It is not possible to translate work of this kind, done under laboratory conditions, directly into practical improvements, and I submit to the aluminium alloy producers, to the welders, and also to founders, that they should study this series of papers, and particularly the present three, and so obtain a lead as to how they may overcome some of the difficulties which are encountered. Further, I believe that the results are of very much wider general application than only to the aluminium alloys. A small amount of similar work would probably confirm that the basic principles set out here are applicable to the alloy systems of many of the other metals.

Finally, I would submit to the Institute's appropriate Committee that some of the terminology which has troubled this team should be standardized. Each paper has had to define certain phrases in terminology—"hot shortness", "hot cracking", "hot tearing", "sub-solidus cracking", and so on. It would be of very great service to have standard terms for these and other related phenomena.

The SECRETARY: With regard to the comments of Dr. West on the matter of nomenclature, you may be interested to know that some time ago the Council of the Institute, in association with certain other metallurgical societies—the Iron and Steel Institute, the Institute of British Foundrymen, and the Institution of Mining and Metallurgy—approached the British Standards Institution to request them to take over this question of studying nomenclature and standardization of terms. Within the last week I have received a letter to say that the British Standards Institution have agreed to this request, so that I hope that Dr. West will put such comments as he cares to make to that Institution.

MR. D. C. G. LEES,* M.A. (Member) (contribution read by Mr. J. C. Bailey): The papers now under discussion form the culmination of the work carried out at Birmingham University under Dr. Pumphrey, and it gives me pleasure to note the wide measure of agreement that exists between this work and that which I myself conducted on hot tearing in the laboratories of the British Non-Ferrous Metals Research Association. My own work derived from efforts made during the war to assess the casting characteristics of some of the aluminium foundry alloys. It was natural that it should begin with a comparison of commercial alloys, proceeding later to the simpler binary alloys. Dr. Pumphrey's work, on the other hand, has moved along lines which, intellectually speaking, must be regarded as more satisfying, since it proceeded from the simple to the complex.

In spite of these differences of approach, however, the two pieces of work seem to have reached very similar conclusions. Broadly speaking, it appears that the hot tearing of aluminium alloys during freezing under restraint is governed principally by constitutional factors, easily explained by a consideration of the process of freezing in solid-solution alloys. In both Dr. Pumphrey's and my own work it is agreed that the danger of tearing arises only when a coherent network has been formed by the growth of the interlocking arms of the dendrites.

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On general grounds, supported by experimental evidence, it is to be expected that tearing would take place above the solidus, so that there is a critical range of temperatures. Any factor which shortens this range will decrease the hot-tearing tendency. In my work it was pointed out that the higher the eutectic content the longer is the formation of a coherent network delayed. This suggestion led to the conception of the eutectic index, which proved valuable in dealing with the complex alloys met with in foundry practice.

In Dr. Pumphrey's work, his refined methods for tensile testing at high temperature have shown the existence of a brittle range within the liquidus-solidus interval. Because of the interest in welding which was fundamental to Dr. Pumphrey's work, the lower ranges of alloying concentrations were studied, and the region of decreasing resistance to hot tearing was delineated. Less emphasis was laid on this range in my work. It was noted, however, that the hot-tearing tendency of commercial-purity aluminium was greater than that of super-purity metal, and this was ascribed to differences in freezing range.

The constitutional factors are no doubt the most important in determining the incidence of hot tearing, but two other minor ones must be considered. These are grain-size and gas content. The grain-size effect is explicable in terms of the stage at which a coherent network of primary crystals is formed, while the effect of gas may be regarded as being due to a redistribution of residual liquid. The views expressed by Dr. Pumphrey and his co-authors and my own views are in substantial agreement on this point, although a slight difference in scale is envisaged. Grain-size and gas-content effects, and particularly the latter, are probably the least satisfactory part of the picture, and it is to be hoped that further study of them will be possible.

A word should be said about the experimental methods used in Dr. Pumphrey's work. Some criticism has in the past been brought against the ring-casting test used by Dr. Pumphrey and his collaborators, and I prefer the graded series of test castings which I have myself used. Nevertheless, it should be pointed out that in the Birmingham University researches the ring-casting tests did not stand alone; they were supplemented by high-temperature tensile testing experiments. The methods used for this work are most elegant, and will appeal to all those who have been concerned in the difficult matter of determining the tensile properties of test bars during cooling in the mould.

MR. J. C. BAILEY,* B.Sc. (Member) : The authors have been commendably bold in attempting to bridge the gap—and it too often is a gap—which exists between the academic and the practical use of metallurgical investigations. They have employed laboratory methods and have attempted to interpret what the significance of their results may be in welding processes, and even in the foundry. To my mind, that is a true function of workers in an industrial metallurgical laboratory. It is bound to lead to a good deal of comment and criticism on both sides, and that has already been evident, but it is a very healthy state of affairs.

In the third paper presented this morning, Dr. Pumphrey and his co-author suggest that cracking below the solidus is affected by the extent to which cracking may have occurred above the solidus. I should be grateful if they would indicate how that influence is considered to operate—whether it is that a crack forming in the early stages of cooling acts subsequently as a stress-raiser, or whether it operates by some other mechanism.

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MR. W. A. BAKER,* B.Sc. (Member) (contribution read by Mr. R. W. Ruddell): I should like to comment on one point discussed by the authors in their paper on the factors affecting brittleness above the solidus. On pp. 246-248, the authors seek to show that the healing of a hot tear is a rare occurrence, only likely to be met with when the site of the tear adjoins an ample source of feeding liquid. This is undoubtedly true of the large tears with which the authors are mainly concerned; it is certainly not true of small tears, as I have shown in my paper† on micro-porosity in magnesium alloy sand castings. I showed there, to my own satisfaction at all events, that during the early stages of solidification of these hypo-eutectic alloys the pasty mass of primary dendrites and of residual liquid tends to move as a whole to accommodate this freezing shrinkage. The term "mass feeding" has been used to describe this movement. The movement comes to an end when the primary crystals become coherent, but at this stage the primary crystal network is very weak and tends to develop numerous minute ruptures, the ruptures occurring on planes at right angles to the direction of motion during mass feeding. In bars or plates, where the direction of movement is parallel to the mould walls, these early faults develop on planes normal to the mould wall.

At this stage in freezing there is a considerable amount of liquid left in the casting, and I produced evidence showing that the small faults in the dendritic network are healed by influx of residual liquid. The important point about this is that at a much later stage in freezing, when the freezing shrinkage is being fed by interdendritic flow of residual liquid, the slightly larger pools formed from the initial tears feed the smaller pools in their immediate vicinity, and the ultimate result is that a series of shrinkage cavities appear, more or less interconnected, on the plane of the original fault. Obviously this kind of porosity has a most damaging effect on the mechanical properties of the casting.

Fig. 32 of my own paper‡ showed radiographs of two magnesium-zinc alloy test-bars, one of which was well fed and the other poorly fed. The radiograph of the poorly-fed casting contained a large number of white streaks denoting patches of porosity, and a few black marks caused by local segregates of the dense magnesium-zinc eutectic. In the well-fed casting, on the other hand, there were naturally far fewer patches of shrinkage porosity, but at the same time there were a larger number of patches of eutectic segregate. I concluded that what had happened was that the feeding liquid had filled a number of tears, so causing these segregates.

One may draw the general conclusion that the susceptibility of an alloy to damage to its mechanical properties by shrinkage porosity is roughly indicated by its tendency to hot tear, a conclusion of considerable practical importance which confirms general experience in the British Non-Ferrous Metals Research Association's work on the casting properties of light alloys. A close correlation is not found, for several reasons, but, speaking generally, one can predict that the tendency of an alloy to hot tear is a good measure of the next most important feature of its casting characteristics, that is, its susceptibility to mechanical weakness if its freezing shrinkage is imperfectly fed. The present authors' views on the occurrence of the healing effect would preclude this useful generalization.

MR. E. VAN SOMEREN,§ B.Sc. (Member): It is with some diffidence that I criticize a work of this nature, because it is so extremely helpful to find anyone investigating the fundamentals of welding in this way. I have been engaged

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† *J. Inst. Metals*, 1945, **71**, 165.

‡ *loc. cit.*, Plate XXIX.

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for two years on the development of welding processes for aluminium alloys; and I must admit that I have had some difficulties in applying the results of this work, chiefly because, although the authors have extended their field from binary to ternary alloys, and in one case to a quaternary alloy, the industrially available wires and plate for welding usually contain at least five constituents, and in some cases six or seven, which I think puts them outside the field of theoretical metallography.

The one criticism which I want to make is that it is necessary to read this series of papers very carefully to find out that they refer only to gas welding. I think that authors who mention welding should specify at once whether they mean gas welding or arc welding, because there are considerable differences in the difficulty of extending welding to these metals, according to whether you use the very fast heating and cooling which are possible in arc welding, or the conditions in gas welding, where there is more chance of feeding a crack and where the thermal gradients are more gradual.

I do not want anyone to feel that this is a serious criticism of the papers as a whole. It may be one more brick for those who are dealing with terminology.

MR. W. I. PUMPHREY (*in reply*): We should like to thank those members who have contributed to the discussion. Dr. West has referred to the aims of the researches now being carried out at Birmingham, and we should merely like to add to his remarks our own hope that the results will be applied in industrial practice in the near future. If anyone does apply them, we should be most grateful for any observations which they may have to make on the correctness or otherwise of our deductions and suggestions.

We agree with Dr. West that it is perhaps now desirable to tidy up the terminology used in our work, and we were very interested to hear Colonel Guilan's remarks on this point.

We should like to thank Mr. Lees for his exceedingly complimentary remarks, and in particular are grateful to him for emphasizing the very close correspondence which exists between his findings and the results which we have obtained. We agree with Mr. Lees that further attention must be given to the effect of gas on the tendency of aluminium alloys to crack at high temperatures during casting and welding, and in fact it is hoped to carry out further work on this point in the near future. The further work on the effect of gas content on the tendency to hot tearing should also provide some information on the probably associated phenomenon of porosity in the weld bead and in the weld area during the welding of aluminium alloys.

We should also like to thank Mr. Bailey for his remarks. The question of the effect of cracking at temperatures above the solidus on the cracking which occurs at temperatures below the solidus can be considered in two ways. Firstly, if the cracks that occur above the solidus are small and narrow, they will tend to act as stress-raisers at low temperatures in alloys caused to solidify and cool under restraint, and will so give rise to considerable low-temperature cracking if the alloys are of low ductility and cannot accommodate the increased stresses at the ends of the cracks by local deformation. If, on the other hand, the cracks which occur at high temperatures are large and wide, it is thought that the stress concentrations at the ends of the cracks will be small, so that even in alloys of relatively low ductility large cracks which form at temperatures above the solidus will tend to open out gradually under the contractional stresses which arise during cooling, and will not give rise to stress concentrations of sufficient magnitude to cause further cracks to occur at lower temperatures. In other words, a large, wide crack opens out under contractional stresses and does not have such a pronounced stress-raising effect as a small crack. The stress concentrations at the ends of small, narrow cracks cause the formation of further cracks.

With regard to Mr. Baker's remarks on healing, we agree to some extent with his conclusions, and in fact have in a very few instances observed healing to occur in small masses. We do not consider that the healing of small tears never occurs, but we do feel that it occurs less frequently in the case of small castings, in which there is no reservoir of healing liquid, than in larger masses where such a reservoir exists. We were interested in his illustration of his remarks, and in his discussion of the correlation between shrinkage porosity and hot tearing. We should like to communicate with him further on this point, because we feel that this may be something which should be considered in our own work, and to which further attention should be given.

Mr. van Someren has pointed out that industrial alloys contain more than four alloying elements and that, in fact, they may contain five, six, or even more elements. It has taken us four years to find out what happens in a quaternary alloy during its solidification, so that the study of the more complex alloys may take more time yet. Actually, however, we are now endeavouring to make a study of cracking in aluminium alloys containing five and more elements, but what is causing most difficulty, at present, is obtaining some knowledge of the constitution of aluminium alloys containing five and six elements. A fairly precise knowledge of the constitution of the more complex aluminium alloys is essential for the interpretation of the experimental cracking results and for their explanation on theoretical grounds. A theoretical explanation of the results is, of course, imperative if our work is to be of any value for predicting the probable behaviour during casting and welding of complex aluminium alloys not as yet examined by either the ring-casting or the restrained-weld tests.

Mr. van Someren's mention of the omission to state clearly in the papers whether our welding processes were gas or arc is well taken, and care will be taken in future papers to make clear whether gas or arc welding has been employed. It may, however, be emphasized that the metallurgical aspects of gas and arc welding are very similar. The two processes merely consist in joining two pieces of solid metal by deposition of liquid metal between them, and we are concerned only with what happens metallurgically in the liquid portion during its solidification. It is felt that the metallurgical happenings must be the same no matter how the liquid metal is deposited. The external factors, such as the rates of heating and cooling, the nature of the fluxes, and so on, will affect the happenings in the liquid metal during its solidification, but I think that if the purely metallurgical aspects of the problem are considered it will be found that the metallurgical problems associated with gas and arc welding are identical. We are now, in fact, working on the problems associated with the arc welding of aluminium alloys; in particular with the effect of the rate of heating and cooling during welding on the tendency of such alloys to crack at temperatures above the solidus, and on the tensile strength of the weld complex and the porosity of the alloys after welding. It has been found, so far, that the deductions made on the basis of gas-welding work are equally applicable when the welding is effected by means of the electric arc.

CORRESPONDENCE.

MR. L. C. YOUNG,* M.Sc. (Student Member): I should like to congratulate the authors on their explanation of the fact that some alloys do not crack, although they possess shrinkage-brittleness, by supplementing the theory of liquid healing with the new conception of accommodation between crystals.

I agree with the authors that flow of healing liquid would be difficult in

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the absence of a convenient reservoir. It seems probable that healing by liquid metal occurs only during the earlier stages of solidification, when there is a sufficient amount of liquid metal present. During the last stage of solidification, when the interdendritic channels are very narrow and hot tearing is most likely to occur, it is doubtful whether the limited amount of liquid along the grain boundaries will be able to heal the cracks effectively. The following reasons may be advanced for this view:

(a) The time taken for the last trace of metal to solidify is only a fraction of a second.

(b) There is a considerable frictional resistance to the flow of liquid metal in the narrow zig-zag interdendritic channels.

(c) The residual liquid metal is likely to have a high viscosity and will not only be reluctant to flow, but will also be incapable of favourable capillary action.

Healing of hot cracks during the last stage of solidification by inflow of liquid metal in the manner postulated by Verö and Lees is therefore unlikely to occur. The minor adjustments, or accommodation between the crystals, suggested by the authors, seems to be the most likely method of "healing".

I am, however, in doubt about the manner of adjustment as illustrated by the authors in Fig. 6 of the second paper (Plate XX). In my opinion the last trace of liquid metal between the crystals, no matter how thin it may be, will act as a lubricant facilitating the sliding of one crystal over the others under contractional stresses. This mechanism would relieve stresses which would otherwise cause hot cracks. It is probable that after adjustment there will be some voids left between misfit crystals. Some of these voids may be filled by liquid squeezed from the grain boundaries, while others may form the internal fissures noted by the authors for an aluminium-zinc alloy on p. 249. If the number of fissures exceeds a certain limit, hot cracking will become apparent.

According to this explanation, the greater the eutectic content of the alloy, the thicker the liquid film between crystals during the last stage of solidification, and so the easier will be the adjustment among the crystals and the more complete the filling of the voids; thus, the alloy will have a lower susceptibility to hot cracking. The evidence of healing of cracks by inflow of eutectic liquid as found by microscopic examination may be the result of adjustment between the crystals.

This reasoning can also explain why a fine-grained structure is less susceptible to hot cracking than a coarse-grained structure. A casting with a fine equi-axed structure has a greater proportion of eutectic liquid at the grain boundary than a coarse columnar structure, in which a large proportion of the eutectic liquid is trapped inside the crystals. The coarse structure is thus more rigid and cannot slip without leaving relatively large voids.

In general, it is probable that above the solidus temperature a thin liquid film will always surround the crystals, and the concept of the formation during solidification of a rigid network of primary dendrites which cracks under restraint and is then healed by residual liquid is misleading. The solidifying metal may have an appreciable strength even if a thin liquid film exists between the crystals. (It is a well known fact that two slip gauges when fitted together are difficult to separate in the direction perpendicular to the slipping planes, but they can be made to slide along the planes. One of the factors leading to this phenomenon has been reported to be the presence of a very thin liquid film of moisture between the gauges.) The continuity of the strength-temperature curves above the solidus temperature, as found by the authors, seems to indicate a continuing decrease of the thickness of the liquid film.

The gradual increase of elongation with decreasing temperature above the solidus during the transition from brittle to ductile fractures, as revealed by the direct-casting and reheated-casting tests, corresponds perhaps to the decrease in thickness of the liquid metal film. This would explain why the higher the eutectic content in the alloy, the shorter is the transition. (See Figs. 19 and 20 of the first paper, pp. 212 and 214.)

It is possible that the crystals themselves could deform to some extent, but in the presence of a liquid film at the grain boundaries it is, in my opinion, unlikely that this could occur to quite the extent shown in Fig. 6 (Plate XX).

In short, slipping along crystal boundaries to accommodate contractional strain, facilitated by the presence of a liquid film, seems the most probable explanation of the phenomenon of hot tearing during the last stage of solidification.

Another point which I should like to mention refers to Fig. 7 (Plate XX). In this Figure, the authors compare four different methods of testing and indicate that the ring-casting test has a high power of differentiation between the degrees of hot-shortness of alloys. I should like to mention that by modifying the shape and dimensions of the ring-casting mould, the sensitivity of the test can be considerably increased. I think the most advantageous feature of the ring-casting test lies in the fact that the length of cracking is proportional to the degree of hot-shortness of the alloy. This is a point which is brought out not only by experimental results, but also by theoretical reasoning, and it is not shown in other methods of testing.

The AUTHORS (*in reply*): We have read Mr. Young's comments on the three papers with considerable interest, and we should like to thank him for his very thought-provoking remarks. We would, however, suggest that for any understanding of the phenomena associated with the solidification of liquid metal, it is more logical to think of the solidifying mass not as containing large numbers of geometrically perfect crystals which can "slide upon one another" but as containing initially a large number of nuclei from which irregular dendrite growth begins. The behaviour of a metal cooling from the liquid to the solid state must depend upon the way in which the still-liquid portions of the solidifying mass are entrapped between the growing dendrite arms.

If the solidification process is considered in this way, it will be seen that no real comparison can be made between the strength possessed by a dendritic network and the force required to pull two slip gauges apart, since the strength of a dendritic network must be due, in very considerable measure, to the interlocking of the dendrites. The gradual increase in the strength of an alloy, which solidifies over a range of temperature, with decreasing temperature above the solidus may be evidence of a gradual increase in the degree of dendrite interlocking just as well as evidence of a continuing decrease in the thickness of the liquid metal film between the crystals. On the basis of present knowledge of the way in which solidification proceeds, the former explanation would seem to be the more correct.

We are grateful to Mr. Young for emphasizing the value of the ring-casting test for estimating the susceptibility of aluminium alloys to crack at temperatures above the solidus during casting and welding. In this connection we might mention that work carried out since the publication of the three papers has confirmed the usefulness of the test for estimating the susceptibility of alloys to crack when welded in industrial conditions. We have also found that the range of sensitivity of the ring-casting test can be varied by alteration of the dimensions of the ring-casting mould. The dimensions we have adopted for the mould are, however, designed to permit maximum differentiation of the sensitivity to cracking of the greatest possible number of aluminium alloys.

SYMPOSIUM ON METALLURGICAL ASPECTS OF NON-FERROUS METAL MELTING AND CASTING OF INGOTS FOR WORKING: GENERAL DISCUSSION.*

(*J. Inst. Metals*, this volume, pp. 285, 311, 325, 339, 353, 373.)

PROFESSOR H. O'NEILL,† D.Sc., M.Met. (Member of Council) (*Rapporteur*): In the old days when some people drew a distinction between ferrous and non-ferrous metallurgy, I well remember the departure of one of our Past-Presidents, the late Mr. W. R. Barclay, from Sheffield to Birmingham to cast non-ferrous metals. There he found it very practicable to introduce some of the well recognized procedures that were used in Sheffield for steel-making. In some respects Metallurgy is indivisible, and throughout this discussion I for one shall be watching what the non-ferrous metallurgists say in comparison with what might be contributed by those concerned with ferrous procedures. As one looks through the papers the thought arises, How would a steel metallurgist put these things? One might expect, for instance, that regarding fluxes, degassing, and reactions of slag with metal the texts would contain some physical chemistry. It is recognized that at the higher levels thermodynamics may be brought in and one might enquire whether it appears in the present papers. If not, are our authors not briefed in this subject, or do they want to be really practical and keep their feet on the furnace floor, or do they not think sufficiently along such lines at the present time?

Starting with the charging of metal one might expect something to be said about the purity of the materials to be melted, and perhaps their size and shape. How much shall we hear about furnaces, fuels, and melting atmospheres? To what extent has the pyrometry of liquid metal in non-ferrous foundries received attention? On the casting side of steel works the pyrometry of liquid steel now seems to be in a pretty ship-shape condition. In looking through these papers I have kept an eye on the extent to which pyrometry is used, and while some authors employ instruments realistically others say that temperature judgment can be left to the melter. This state of affairs needs consideration.

The macrostructure of ingots affects the quality of the resulting wrought material, and we shall seek in the papers for information as to how macrostructure is controlled. Do we find that the authors are conscious of the effect of nuclei when freezing takes place, and do they appreciate fully the question of thermal gradients in the moulds? All the papers, I think, refer to the dressing of the moulds. There are some very interesting points regarding the way in which these dressings can affect the macrostructure, and we soon get into fields where highly scientific factors are at work.

It is not my duty to discuss the papers. I am only here as a sort of head waiter to run through the menu of the feast that has been set before you. Sometimes a head waiter has to explain the meaning of the items and emphasize the sauces. I do not think that is necessary in this particular banquet, because the papers seem to be written in homely terms and are so straightforward as to be of the cookery-book type.

* Discussion at the Annual General Meeting, London, 31 March 1949.

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Taking them in turn, for the "outer works" we have the excellent general review on the casting of metals by Messrs. Bailey and Baker. These authorities seem to have described all the ills and troubles that might arise in this particular job. In fact, you wonder how it is possible to make successful ingots when you read about the dangers and difficulties. But they tell us how to do it, and one may note the tribute paid by some of the authors in the Symposium to the work of these two researchers.

I would like to underline the advantages of water-cooled copper moulds upon which the authors insist, and which I think they pioneered in this country. Their advocacy of copper moulds is supported by most of the subsequent papers. Plate XXVII is a photograph illustrating surface folds on a brass ingot. I suggest it would have been exciting if we could have prepared a stereoscopic picture of that particular specimen. In Mr. Bond-Williams's paper there is a picture in gorgeous technicolour. I understand it is not the first time that our *Journal* has been so embellished, but it is quite striking. Perhaps on some occasion we might try a stereoscopic picture in colour. One would need coloured viewing screens, and I think that these might be supplied by the Institute on receipt of a member's Banker's Order.

The authors point out that to avoid surface folds we require a high casting temperature, a rapid pour, a vertical mould, and a central stream of metal. I wonder how many of the melting shops dealing with non-ferrous alloys insist on these four points in order to get a good surface. Most of the papers before us to-day endorse these recommendations. The question has been asked whether there should be a high casting temperature or a medium casting temperature, and the same question has arisen in connection with ingots of steel. The present authors suggest that a high casting temperature with a rapid pour is best.

This first paper discusses the effect of gases, and on p. 288 we read about the superficial defects which can arise from subcutaneous cavities. In the metallurgy of steel one has just the same sort of trouble. Subcutaneous blow-holes are liable to develop just below the skin of steel ingots, and lead to defects in the surface of the finished material.

The authors have a good deal to say about the hydraulics of casting and non-turbulent pouring. New methods of continuous or direct casting are emphasized which receive great attention in subsequent papers. Messrs. Bailey and Baker remark that apart from the original Durville publication describing tranquil pouring, there has been no description of the industrial use of the method. Fortunately the omission has been remedied in the present Symposium with a paper by Murphy and Callis, and a reference by Dr. Cook. The accounts given of degassing processes recall the production of "killed" and "balanced" ingots of steel. The reference on p. 309 to the powerful grain-refining effect of small additions of certain elements reminds one very much of the production of steels of controlled inherent grain-size. Since this latter subject is still one for research and discussion, it might be that information developed in the non-ferrous field will be of general use.

We next come to the paper by Mr. Waddington describing the production of high-conductivity copper shapes in Ontario. This is a detailed account of how to do the job in a modern way. It might be mentioned that in Canada and the United States labour costs are higher than in our country, and therefore the expenditure of a lot of capital for labour-saving is probably justified by the more economical results. Molten blister copper is refined in 300-ton reverberatory furnaces to make anodes. The anodes are then electrolysed to make pure cathodes, which are melted and cast into special shapes for industry. The melting is now done in 30-ton 3-phase direct-arc furnaces, connected by launders to enclosed pour hearths having a capacity of 5 tons. The pour hearths are themselves heated by induction methods. The linings of the

furnaces are mentioned in only a few words. They are essentially of magnesia, and it would be valuable if we could learn more about them and their life.

We are told how the oxygen content of the copper is adjusted by drawing air through the melting chamber. The passage of this air is controlled so that after its reaction with the graphite electrodes of the furnace, the atmosphere consists mainly of carbon dioxide and nitrogen. By this means the oxygen content of the copper bath is adjusted.

The paper describes a shining example of a modern plant having a very high degree of scientific control. The product has to be free from inclusions, fissures, blowholes, laps, and so on, and the control in melting, together with a balanced rate of ingot solidification, is claimed to bring the right results. Pyrometry seems to have received very special attention. The molten metal temperature is measured with continuous recorders, and mould-temperature control is effected by automatic regulation of the cooling water. For special low-temperature casting work the lips of the ladles are electrically heated. The methods of record and of inspection show such thoroughness that one can hardly expect any niggers to be found in the woodpile. I think we have an example here of a first-class up-to-date plant where the conditions justify the expenditure of a good deal of capital.

The third paper, by Messrs. Murphy and Callis, is a special study of the production of aluminium bronzes. Unless these excellent alloys are cast with very great care and experience, the results obtained with them can be very disappointing. They have a narrow freezing range, and this produces difficulties regarding feeding, with the liability of getting a central pipe. The liquid metal also becomes coated with a tenacious invisible oxide coating which seems to fit it like a nylon stocking. You must not get this film damaged or the fragments become entangled in the ingots and mechanical properties deteriorate.

We are told in great detail how to cast these alloys to avoid these ills, the method being, of course, the Durville process. In particular a machine developed in their own works is described having a special feeding dozzle introduced between the melt container and the mould. The tenacious oxide film which in so many respects is a nuisance has the advantage that it prevents hydrogen from producing pinhole defects, and so the authors point out that the use of fluoride fluxes which might remove this film is a disadvantage. The authors also describe the bottom running of ingots as a process patented by Durville, and this, of course, reminds one very much of some of the steel-works practices. Finally, they mention the routine Brinell testing of the final ingots as a control of composition.

The fourth paper is by Mr. Bond-Williams and pays tribute to Messrs. Bailey and Baker, whose publications convinced him that works practice could be improved. It took a good deal of time to complete all the alterations. The original coke crucible melting furnaces were modified and the casting technique was improved by the development of a special pouring ladle with a tundish to control the rate of mould filling. The title of the paper emphasizes special flux-degassing, and yet when one comes to look at the text there is really not a tremendous amount said about that very interesting and very important procedure. I think it would be helpful if we had something about that in the discussion, and perhaps afterwards the author could say more. What is done, of course, is to produce an oxidizing slag containing copper mill scale. That gets to work, and excess oxidant is removed by adding an excess of phosphorus in the form of phosphor-copper. Temperature measurement is spoken of, but no particular views are expressed as to how it is to be done. If anybody can tell us something about the thermodynamics of the degassing process I think it would increase the value of the Symposium.

From the coke-fired crucible furnace we come to the paper by Messrs.

Cook and Fletcher, which describes the melting of brass in low-frequency induction electric furnaces. These operate something like the Talbot process in steel works. You prepare a melt and pour out a large proportion of it, but you leave some in the furnace. Then you add more solid metal and prepare another cast. The advantage of the induction furnace from the point of view of natural mixing of the metal is mentioned, especially in connection with the production of leaded brasses. The authors point out that with their alloy degassing treatments are not necessary, for the high vapour pressure of the molten zinc reduces the solubility of gases. In the melt the zinc which is inevitably present also acts as a deoxidant, so that nothing need be done in that connection. Special attention has been paid to metal losses, and it is claimed that they can be kept below 1% if proper precautions are taken. Special attention is also paid to moulds, mould dressings, and casting temperatures. The authors are very precise about the latter, and a latitude of $\pm 10^{\circ}$ C. is spoken of. Table I gives quite precise optimum values for alloys of different copper contents. The question of segregation in the ingots is also mentioned, and I think that this is the only paper which deals with the point. We are given some tests which can be applied to the wrought product to see whether the segregation is of important dimensions.

The last paper is by Messrs. Bradbury and Turner, and it deals with the production of nickel-brass alloys in oil- and coke-fired non-tilting crucible furnaces. Their plant is obviously of the older type of equipment, but they have developed an oil-fired furnace, and give us a complete drawing showing the design of the installation. Two oil-fired with two coke-fired furnaces produce as much metal as five of the coke-fired furnaces, and that is what the paper is largely about. Very full particulars are supplied of the working of the shop. Although zinc is present in these alloys and we have heard as regards brass that it suffices as a deoxidizer, still in making nickel silver these authors add manganese and phosphor-copper as deoxidants before casting. No pyrometric control in the scientific sense is admitted, but a stirring test and indications of zinc boil suffice for an experienced caster to decide when the melt is ready to pour. Water-cooled copper moulds (as usual) are advocated, and feeding of the ingots is carried out with dozzles and the other devices which follow the general lines of metallurgy.

My time is up. I have merely tried, as I said, to be the head waiter. I hope I have not done injustice to the cooks and the other people who have worked behind the scenes, preparing this feast for us. They will have a chance at the end to underline anything of importance that has been omitted; and I hope that these remarks will serve to catalyse an interesting discussion.

MR. A. L. MOLINEUX * (Member): May I begin by saying this is the first time I have opened a Symposium, and I trust that you will look upon me with a lenient eye.

I think, if I may say so, that the Institute of Metals is to be congratulated on this Symposium. They have answered the criticism which has so often been levelled against them about the lack of practical papers. I do believe it will enhance the prestige of the Institute very greatly.

I would like to discuss two papers—the one by Mr. Bond-Williams and the one by Messrs. Cook and Fletcher. I consider that the flux degassing of phosphor bronzes is one of the greatest achievements in the last twenty-five years in metallurgical practice. Prior to that we applied rule of thumb methods, and it is quite obvious we did not know what we were doing. We got no further until the development of this method. The credit for the basic work must, of course, go to Genders and Bailey, and for the practical application—in my own experience, anyhow—to the Tin Research Institute.

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I would congratulate Mr. Bond-Williams on his paper, although I cannot go all the way with him; but then he would not expect me to, of course. He speaks of improvements in the last ten years, and he quotes the Wigley furnace as an improvement. I knew the Wigley furnace twenty years ago, and I spoke to my Chairman, Mr. C. C. Bamford, who is known to many of you, and he knew it thirty years ago. Wigley made great play about air being supplied at normal outdoor temperature and humidity, and he insisted on air being carried in from the outside. We did that with a 9-in.-dia. duct in the floor and were very pleased with the results. Some time afterwards we had occasion to go down below and found it had been stuffed up with charcoal bags so concluded that it did not have any very great effect, after all, on the quality of the casting.

Mr. Bond-Williams quotes figures of half a ton of coke per ton of phosphor bronze with the old method and $4\frac{1}{2}$ cwt. to-day. I am afraid I cannot agree with either of these figures. I feel that the one is very high, and I would be very happy to achieve the other even under to-day's method of casting. I hate to confess it, but our average weight of coke used per ton of all our metals cast in the last three years has been $6\frac{1}{2}$ cwt. That, of course, includes quite a lot of rich metals; but, even if we assume that the rich metals take more than $6\frac{1}{2}$ cwt., it would still bring the phosphor bronze well over $4\frac{1}{2}$ cwt. per ton of metal cast.

As to pouring troughs, we have found that if we use a cast iron tundish with the bottom slotted and use Morganite troughs which we can easily get to shape, there is a great advantage inasmuch as one can pre-heat them and they are easily repairable if the holes begin to wear. It is quite easy to go round the holes with one of the well known refractories. I consider that the pre-heating of the Morganite lining has great advantages.

Mr. Bond-Williams quotes figures for his crucibles of up to thirty-eight heats, but a more economical way we have found is to use them on phosphor bronze for the first twenty-five and then change them to brass. You will find your crucible expenses are cut very largely in that way.

As regards mould dressing, we have come back to a very thin dressing of French chalk and tallow. We have tried aluminium, but there was more aluminium paint on the floor than on the moulds, and we did not obtain a very satisfactory result.

To sum up the old method and the new, I would say the general quality as regards soundness is generally much improved. The surface quality is very much enhanced. As for tensile elongation and hardness, we never had any difficulty before, but that may have been because we never went above 5% tin. We have not cast the higher-tin-content phosphor bronzes. The greatest saving has been the reduction of scrap. I am sorry to say that we used to make anything up to 50% of scrap in the old days of tin sweat, and now we are down to a very much more reasonable figure—I would say, including process scrap, of the order of 25%. Of course, there is no cost for machining now to get rid of the tin sweat, not that that was very satisfactory, because it merely exposed the porosity underneath.

That is one side of the picture, but there is another which I came across quite by accident the other day. We use pickling trays for the pickling of our ordinary brass and copper strips. They are made on the principle of the ordinary doormat scraper, slats across, and four supports on either side, picked up by an overhead crane. We used phosphor bronze for them, cast by the old method, and the slats were $\frac{1}{8}$ in. thick by 2 in. wide, standing on edge with spaces between, and the metal stood on them. We found that although they did not corrode, they were very subject to mechanical damage going round the mill. They were being bumped into obstacles and we decided about eighteen months ago to renew some of them and use slats $\frac{1}{2}$ in. thick. For them we

used phosphor bronze cast by the modified method. The original ones, cast in the old way, have lasted ten years; and as far as the micrometer can tell us, there is no appreciable corrosion. But those made of phosphor bronze cast by the new method have wasted 0.050 in. in eighteen months. I cannot explain it: I can only tell you it is a fact.

There is another point that I think is of interest, if I may bring it up. It has not quite to do with the casting of phosphor bronzes, but it concerns the casting of a similar alloy by means of this modified process. It is a problem which has been put up to the British Non-Ferrous Research Association and to the Tin Research Institute. Both of them investigated it with the thoroughness which they always display, and they could not supply the answer.

In the textile trade there is a call for gun-metal tube: 90 copper, 2½ tin, 1½ lead, and 6% zinc. It must be perfectly concentric and must have very little frictional resistance to the cotton as it spins round. To get the concentricity we have to make it out of gun-metal strip brazed up in the form of a tube. [Specimen of finished tube exhibited.] It is turned into an open-joint tube, put in a furnace with flux and the solder, and then brazed. The resultant joint looks like this specimen I have here. It is then pickled and cleaned off and drawn. The scrap on it was very high—anything up to 50%—because we used to suffer from tin sweat very badly, and I have here a particularly bad example. Naturally when this modified method came into being, we went over to it for the gun-metal. The melt came out with an excellent surface. But when we came to braze it in ten-foot lengths it twisted as it went through the fire and caused the joint to be broken in several places. You would naturally say that the cause of the twisting was internal stress, and the obvious thing to do would be to anneal the metal to relieve the stress before putting it into the brazing furnace. This we did, but the twisting still occurred. We called in the two Associations and they could not help us, and then quite by accident I dropped on the answer.

What I am concerned with to-day is to find the explanation of what works in practice. Previously we used to cast two 1-cwt. strips: the first was cast with four holes, 0.187 in.; the second with four holes 0.203 in. We got this twisting effect which made it entirely useless, and we had then to revert to the old method consisting of seven or eight holes of ⅛ in. and had to put up with the resultant tin sweat. Then we thought we would try gradually increasing the holes using the modified casting method, and we find to-day that we can successfully cast the material without any appreciable tin sweat and without twisting by using five holes, 0.203 in. diameter. I do not know why. I would like to know whether any gentleman here can offer an explanation of that phenomenon.

The paper of Dr. Cook and Mr. Fletcher I will discuss next, and my remarks will be confined to pit furnaces. When you get a gentleman of the academic distinction of Dr. Cook and a gentleman of the vast practical knowledge of Mr. Fletcher, they can, indeed, produce a formidable paper, and I can only wish this paper had been produced twenty-five years ago. It would have saved me much work and worry.

I agree entirely with what the authors say on p. 354:

“The fact that the production of high-quality shapes substantially free from defects is not always universally and consistently realized, however, is not because of any serious technical difficulties in the processes or unsolved major metallurgical problems, since, in general, for most of the alloys in this category these no longer exist.”

The obvious question is, why do we get faulty brass if that is the case? If we are honest we must admit we do. And when I say “we”, I do not mean

only a small company like ours. We buy several hundreds of tons of brass strips in the year from four other large manufacturers, and we get a percentage of trouble from them just the same. It certainly cannot be ascribable to ignorance on their part of proper methods of casting. I am not really surprised that we do get faults, because as I see it casting consists of a series of operations, each of which, though simple in itself, must be carried out correctly if the final product is to be satisfactory. The other evening when I was looking through this paper I sat back and visualized our casting, and I jotted down thirty different ways in which casting could go wrong—thirty simple little operations which have to be carried out from the time you begin to charge the metal in the pot until you finally deliver it to the rolling mill. Many of these are, of course, listed in the paper of Messrs. Cook and Fletcher. First among all troubles I would put dirt. Cleanliness must come before godliness in the casting shop, and I believe lack of cleanliness is the greatest single cause of trouble in any of our casting shops. If we agree with Cook and Fletcher that there is no metallurgical problem, it can only be a human problem. And I do suggest that casting is hot, heavy, and dirty work. It should be well paid for, and we must get the caster to have a pride in his work by making him appreciate the vital part he plays in our production. In other words, to my mind since most of the metallurgical problems have been solved, it comes down to good management in the casting shop. Think of the day's work of the ingotman. Twenty-four times a day he has to strip his moulds, clean them off, cool them down, dress them, hook them up, and so on. Can you wonder if things go wrong?

I would like to remark here that I consider the rolling industry is very much handicapped by having to work to British Standard Specification 265. I consider this is very ill-chosen because the copper figure is fixed at $61\frac{1}{2}$ to 64, which brings it right into the alpha/beta class, and we do get considerable trouble with beta stringers.

On crucibles, Messrs. Cook and Fletcher refer to their being seasoned and treated when new. I would like to ask how they do it. When we receive crucibles from the makers we put them in an annealing furnace which is not being used. This furnace is one of a pair and the other one being alight maintains the crucibles at an even temperature. We leave them there until they are wanted. They are then taken to the casting shop, brought up slowly to red heat with a fire which comes up with them. But in spite of all this care I have known crucibles fail after two heats, others go thin round the bottom after six heats, with small holes coming in all over them, and if you have the crucible makers in all they can tell you is that the cause of failure is thermal shock. I would like to know what thermal shock is, because it seems to produce a wonderful diversity of symptoms.

Finally, I cannot resist this. On p. 355 Messrs. Cook and Fletcher say:

“Again, the presence of iron is beneficial in reducing the tendency of leaded alpha/beta brasses to crack on hot rolling.”

To one of these gentlemen—I will not say which—I would put the question whether he recognizes this? It is a piece of brass and inside it is half a poker, 1 in. wide by $\frac{1}{2}$ in. thick. Could I ask him if in his opinion this is beneficial in reducing the tendency of alpha/beta brass to crack on hot rolling?

MR. CHRISTOPHER SMITH * (Member): I should like first to offer a tribute to those whom I might call the “Old Masters” of brass casting. We are told brass was first cast in Bristol in this country in about 1700, and certainly it was being cast in Birmingham very shortly after that time. It

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has always seemed to me to be fortunate, looking back, that brass was such an easy material to cast, because I can just remember the amazing shapes into which it used to be cast prior to the 1914 war. It was not uncommon, in those days, to cast tube shells about 5 ft. long by $1\frac{1}{2}$ in. dia. with walls $\frac{3}{8}$ in. thick, five out of one pot, and tubes were made from those castings. Subsequently, this process had to be refined. Similarly, thin strips were cast in inordinately long lengths of fairly poor surface and invariably with considerable cavities on the inside. I am sure the minds the "Old Masters" brought to the problem of casting brass were more opportunist than scientific, but I think that we owe to them, this morning, a meed of praise and admiration and appreciation for the courage with which they attacked this new problem.

I know that in those old days, as I have already hinted, there was no basis of science at all, and the thing that was most precious was what the Americans have so aptly to-day called "know how". This resided very largely in the waistcoat pockets of foundry foremen, and I think we might very aptly call that age in capital letters and in quotes "The Age of Red Phosphorus".

Gradually we began dimly to appreciate that there were certain principles which we were flouting consistently in the manufacture of brass, and that a good many of our troubles were due to that factor of ignorance.

I would like first to comment on the paper of Messrs. Bailey and Baker, which sets out admirably the remedies for all the mistakes we have made in the last eighty or a hundred years. It does seem to me that here is an excellent text-book for all of us from which each of us can learn our lessons. In my opinion we have not learnt our lessons. I feel that I detected in many of the papers a certain air of complacency, a feeling that we had perhaps achieved the ideal and that there was nothing more for us to do; that all the metallurgical problems were solved and that in fact we knew most of the answers. I feel very strongly, and have done for a good many years, that we do not know all the answers and that we have a considerable distance to go before we are able to produce very fine castings, castings of superfine quality; before we are able to solve the problems of high scrap losses, which are colossal in our industry and which in my opinion ought to be reduced materially. In addition, we have to solve the problem of output per man-hour which again is very bad in our industry.

I immediately felt, when I first heard of the Durville process, that there was something very good and something very sound in this process, and I have felt ever since that when we as an industry neglected the principles which M. Durville gave us we made our first mistake. I read with considerable amusement, if I may say so, in some of these papers—and I am not being critical of them but am trying, if you like, to inspire discussion on my observations—of the necessity for what was called "tranquil pouring", and that in order to get tranquil pouring you dropped a stream of molten metal about three feet through the air on to a rising liquid surface in a mould. I also read of the necessity for achieving a fine macrostructure, and that in order to achieve that, one forced gas from a flaming dressing through metal in order to break up the structure and get a fine macrostructure. It does seem to me that these methods do not smack of the scientific or of the precise.

I am guided to make these observations because of the large experience I have had with the production of aluminium alloys. I would also like to indicate that in the casting of magnesium alloys the problem of oxides is just as acute as it is in the production of copper-zinc alloys. Indeed, these problems are much greater, much more difficult—the problem of shrinkage, the problem of turbulence, the problem of oxidation are all very serious and very difficult in the production of these alloys—than with the predecessors of these alloys.

It does seem to me that the problem was tackled in the light-alloy industry in a much more workmanlike manner.

Bailey and Baker give us very precise information about directional solidification. I feel the only contribution we really made to this problem of directional solidification was the installation of the water-cooled mould, which certainly made quite a difference to the quality of our brass ingots, and the fact that we did not tilt the mould but put it upright. It seems to me we have gone very little further than that in our industry, and I think one of the things we have to aim at is tranquil pouring. And by tranquil pouring, I mean tranquil pouring such as is achieved in the pouring of the lighter alloys. I think this is going to present us with quite a number of problems.

I feel quite strongly that the copper-zinc industry has not brought the attention to the use of refractories that it ought to bring. It ought to be able to pipe metals in a similar way to that in which the other alloys are piped in order to prevent the material from oxidizing. We find, too, difficulties with what Mr. Molineux called dirt. This is, I think, a consequence of tundish pouring, and no matter how carefully you do it you will inevitably get dirt in your casting. You have to learn to pour tranquilly, to pour in order to control your freezing to be truly directional in the way in which the casters of aluminium alloys induce directional solidification, and produce castings in which no two waves of solidification ever meet. That is where your problems arise, and that is where the inferior quality of your castings arises.

I think, therefore, that although a good many of the members here present may disagree very considerably with what I have said, I feel very strongly that there is a necessity for us to address ourselves anew to this problem of producing sound castings. In case people's heads are inclined to shake, however, I would like, in conclusion to say that the enormous increase in output which can be achieved as a result of using properly controlled and proper scientific methods in casting, not only in output per man but in output per cent., will pay enormous dividends. Brass casting has already been described as a hot and heavy job. It does not have to be hot and heavy. It is all a matter of technique, of the application of scientific principles to a product which in my opinion can be improved enormously.

MR. HARRY DAVIES * (Member): I am going to change the scene somewhat from brasses and bronzes and so on and concentrate on the very excellent paper we have had from Canada on copper.

Copper in this country is produced by the hard way that we have heard described by two previous speakers, but if they read this paper on the production of refined-copper shapes, they will find there is a very easy way of doing it, if only one cares to organize it. And you can organize it and the "know how" then entirely disappears, because we can introduce scientific methods and scientific instruments to guide us to produce a very excellent casting.

There are two truisms we might bear in mind in making castings of any description, and the first is that every casting made commercially is unsound. What really matters is the degree of unsoundness. The second is that whatever is attempted—and casting is no exception—it is the detail which wins the battle.

It is rather hard to say in the face of this very excellent paper that every casting made is unsound, because the castings produced by the method described are very excellent. But they are unsound, for you have only to look at Table I (p. 322) where you will see a specific gravity of 8.6. You will

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know that that is not the soundest of copper: the latter being 8.93. It is a simple calculation to work out the amount of unsoundness. However, I would take your attention off the theoretical definition of sound castings and direct it to a more practical definition—that given in the paper of Messrs. Cook and Fletcher. I think they describe it extremely nicely in very few words, and as very accurately. I think it is worth quoting:

“A satisfactory casting may be defined as one which is compositionally correct and which on processing by the appropriate technique yields an acceptably high proportion of marketable material.”

I think we shall have to take that definition as our yard-stick.

The paper on copper is full of detail telling us how things are done. There is nothing nebulous about it. It is straightforward, and we can safely assume that what is written in the paper actually takes place. I want, therefore, to direct attention to one or two of the details that are discussed.

First, there is a description of the method by which the author selects his raw material, namely copper cathodes. Until quite recently it was thought that a cathode was so pure a form of copper that its quality could hardly vary. The paper tells us something different, and the author says that he carefully selects his cathodes. It is one of those details which might make a tremendous amount of difference to a casting; that might add a few per cent. to quality. When one gets all the advantages from these details added up, one will get the finest casting.

I would like to substantiate what is said in the paper because recently I have been attempting to make a quality of copper which has to be very pure. In fact, for the particular purpose for which it is used in industry, the arsenic content must be less than 0.002%, a very small percentage. This led me to examine spectrographically the composition of various parcels of cathode copper, and I found that in a parcel of cathode, if I took twelve samples ten were absolutely pure and had no impurities, but two contained the usual impurities—most of the impurities can be found, in fact, with arsenic as high as 0.001%. They contained lead, iron, arsenic, and so on. The author's method tells us physically exactly what I demonstrated chemically: that there is a difference in the chemical composition of cathode coppers. Incidentally, and this confirms what the author writes, one will find that all your impurities are in the nodules, so if one examines the nodules separately from the main body of the cathode, one can get a cathode which is free from impurities, but the nodules will contain all the impurities.

The next detail I want to refer to is mould dressing. All those engaged in the copper industry know, as far as I am aware, and have known for centuries, that there has only been one mould dressing, and that is bone ash. The paper tells you the characteristics of a dressing for copper which are very incomplete, since the first one that should have been mentioned is that the material must adhere evenly on the mould. The author does not mention that. But the fact that he has missed out some relevant properties is very evident. I do not know whether I shall be contradicted, but I do not know of a substitute yet. There must be a good many chemicals and materials on the market which have the characteristics mentioned in the paper but which certainly do not make a mould dressing for copper. There is lime, and several brands of clay. One will find that these possess all the characteristics named, but they do not make good mould dressings. In fact, they are very, very inferior.

Thirdly, I would like to refer to the use of water-cooled moulds. It is generally accepted for casting all the copper-base alloys that water-cooled moulds are the best. They have many advantages. They eliminate hard physical labour, about which we have heard from previous speakers. But I have often heard the question asked: Why does casting of copper in water-

cooled moulds eliminate the blisters in the finished strip or sheet? Actually it does: there is no doubt about it. If one carries out a simple experiment, taking a bath of copper and pouring half of it into a copper mould or cast iron mould and the other half into a water-cooled mould, one finds that the blisters are absent in the castings from the water-cooled mould, but that they are present in the castings from the other mould.

I am going to make the suggestion, which I hope other speakers will take up, that it is obviously due to the rapid rate of cooling of the copper in the moulds. I think it is so rapid that when the gas is evolved on cooling there is no time for coalescence into big bubbles, and therefore we do not get the blisters. It also may be that you will get rid of your blisters because you cool so very quickly and you may therefore have a super-cooled supersaturated solution of the gas which is not evolved at all. I do not know: I throw it out for discussion.

The paper mentions the use of silver in copper, for the manufacture of water-cooled moulds. Other elements have been added, a common one being chromium.

Lastly, there is a paragraph at the end of the paper (p. 324) which contains the statement that the residual phosphorus content of deoxidized copper might vary from 0.007 to 0.060%. I think that is very misleading for English practice, because if one were to attempt to make deoxidized copper with the phosphorus as low as the minimum quoted, one would be in very serious trouble. I do not think you would thoroughly deoxidize it. The figure is probably nearer 0.02% for English practice. One has to remember, however, that Waddington in Canada is dealing with cathode copper which he melts, and it contains no oxygen. Strictly speaking, he is not deoxidizing, but phosphorizing, hence the term phosphorized copper, which is commonly used in Canada and America.

MR. D. F. CAMPBELL,* M.A. (Member of Council): I think our Rapporteur should be congratulated on his opening statement and his remark that the non-ferrous industry can learn something from the practice in steel works.

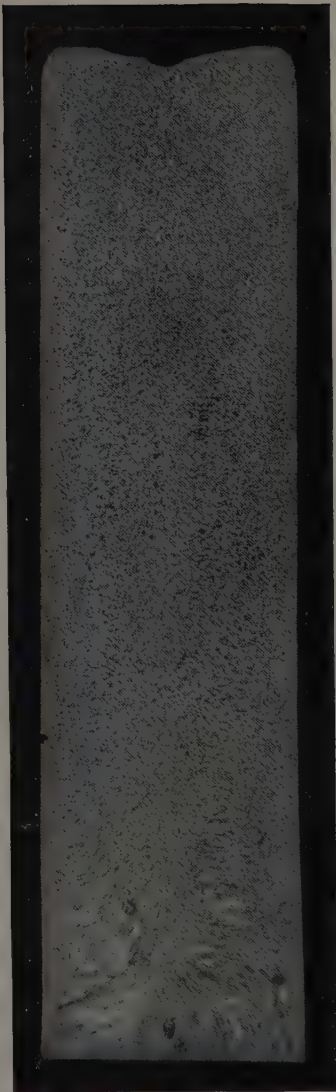
I would like to ask one or two questions about these papers. The paper by Messrs. Bailey and Baker gives a most interesting account of present-day casting methods. I would like to ask them whether they have any record of anybody in England using tundishes working in controlled atmosphere. I have seen very ingenious tundishes with windows of transparent silica in the tops, filled with suitable gases. This has the great advantage, in my opinion, of protecting the stream of metal as it comes into the tundish and during its passage into the ingot mould. I think that is worth consideration.

Mr. Waddington's paper is full of interesting information. I would like to ask him what he means by "chemically-bonded" magnesite bricks. Does he mean that the brick is made by using some special "chemical" bond? If so, I would like to know more about it. Or does he mean bricks are joined together by some "chemical" product?

It was mentioned earlier to-day that the actual expenditure on this plant must be very high. I think that statement can be challenged. In the case of a reverberatory copper-refining furnace heavy expenditure is involved for its chimneys, flues, working platforms, oil tanks, and the large building required. It may be found that an electric installation of this sort does not require very much more capital expenditure than a fuel-fired furnace, taking into consideration the whole of the plant, especially when a new plant is being built. It is perfectly true that a large amount of capital is in the power station, but that is compensated for fully in the price paid for power.

Mr. Waddington states that the temperature is automatically controlled on the pour hearth. In some cases that is done by switching the current on and

* Chairman, Electric Furnace Company Ltd., Weybridge.



B



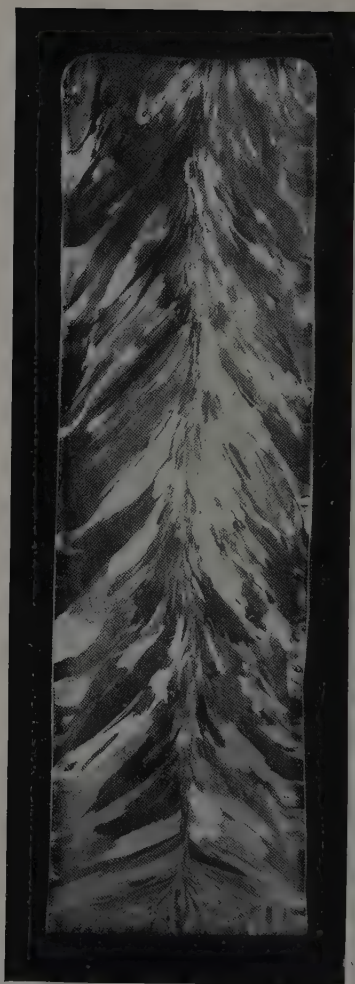
C

FIGS. B AND C.—Structures in Semi-Continuously Cast Aluminium Billets.

[To face p. 1058.]



D



E

FIGS. D AND E.—Structures in Semi-Continuously Cast Aluminium Billets.



FIG. F.—Microstructure of Semi-Continuously Cast Aluminium-1 $\frac{1}{4}$ % Manganese Alloy. Unetched. $\times 75$.

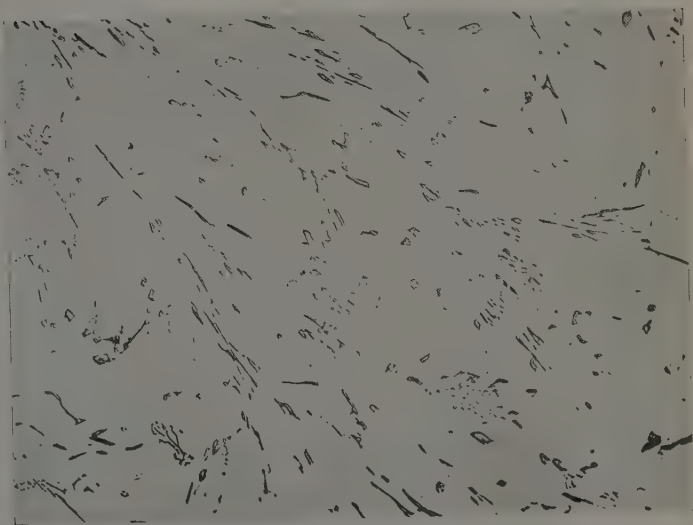


FIG. G.—Same Alloy as Fig. F, Chill Cast. Unetched. $\times 75$.

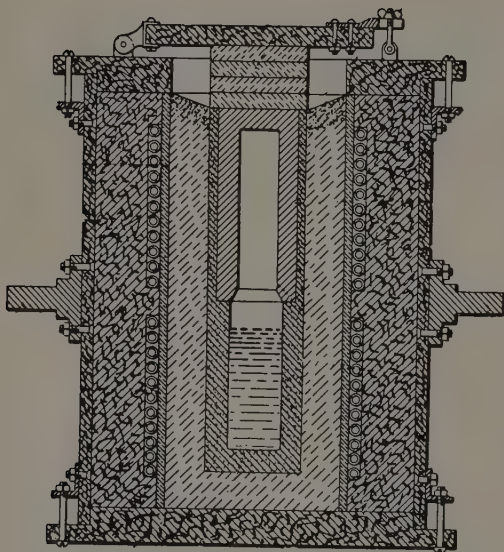


FIG. H.

off or by an auto-transformer that may vary the load on the induction furnace used as a pour hearth. I would like to know a little more about that automatic control, and which method is used.

Cook and Fletcher, on p. 358, refer to the procedure for cooling down and reheating induction furnaces requiring special care. It would be interesting to have a little information on what procedure is recommended in this case. In France, where there have been frequent stoppages of electricity, especially in the Paris area, the precaution taken is that whenever possible the furnace is left with a certain amount of liquid metal in it, so that the channel as it cools can be fed by the liquid metal from above. That avoids the breaking of the channel which is the cause of the trouble in starting up cold furnaces. Another matter that has been mentioned in connection with induction furnaces which would be extremely valuable is experience on linings for melting pure copper.

On the Bradbury and Turner paper, I would like to ask why crucibles are still used, whether coke or oil-fired, for melting nickel silver. An eminent metallurgist a short time ago stated that the thermal efficiency of a coke or oil-fired furnace was about 3%, which should shock our fuel-efficiency investigators. I would like to know why it is necessary to melt these metals in a plumbago crucible, which may be described as a porous pot from which gases can enter the metal, when other methods, such as high-frequency furnaces, are available where there is no risk of contamination by objectionable gases. There are many references in these papers to the removal of gases. I would like to ask whether in some cases we should not do more to prevent the gas from getting into the metal rather than take a lot of trouble to get it out, after we have let it get in. In other words, we ought to be profoundly dissatisfied with many of our melting methods at the present time. I think the paper on the melting of copper shows a great advance on what has been done in past years.

There is one very serious omission, I think, in this paper: so little is said about the melting of aluminium and its alloys. From recent discussions with people in various countries—France, Switzerland, Scandinavia, and this country—it is evident that there are great differences of opinion and that a great variety of equipment is used for melting aluminium. It is obvious that the melting of aluminium metal for slabs, which requires tranquil casting, is quite different from that of some of the alloys. For instance, the mixing of alloys of nickel and chromium with aluminium involves superheating the aluminium, and obviously this requires violent mixing to get adequate homogeneity with metals of such different melting points and specific gravity. A similar case is the making, in the steel trade, of magnet steel which is rather like porridge and contains a large amount of aluminium. In that case the motion in the bath is of particular importance. There is little mention in the papers of controlled movement of metal during melting, and it should be realized that it is possible to regulate movement to a very large extent in liquid metal.

Lastly, I do not think there is enough in these papers about modern equipment for carrying out the various operations or about the possibilities of melting and casting in controlled atmospheres. It would be of great advantage if at some future date we could have a discussion on the correct way to melt aluminium and its alloys, with special emphasis on the equipment involved and methods used for controlling atmospheres and movement of metal during melting and casting operations.

MR. H. W. L. PHILLIPS,* M.A. (Member): In their paper, Messrs. Bailey and Baker refer briefly to the semi-continuous method of casting which is now

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so extensively employed for aluminium and its alloys. As they correctly state, the process is capable of giving blocks of great soundness, with directional solidification, and its advantages, both economic and technical, are in fact so pronounced that much time and effort have been extended in overcoming its chief drawback, namely the development of internal stresses of magnitude sufficient to cause cracking.

The apparatus in general use consists of a shallow, thin-walled mould, the base of which is lowered at a uniform rate as casting proceeds. Cooling of the mould and of the billet is achieved by a liberal supply of water. The solid-liquid interface is dished, and lies only a short distance below the free surface, so that feeding is good and there is every opportunity for the escape of gas liberated during freezing.

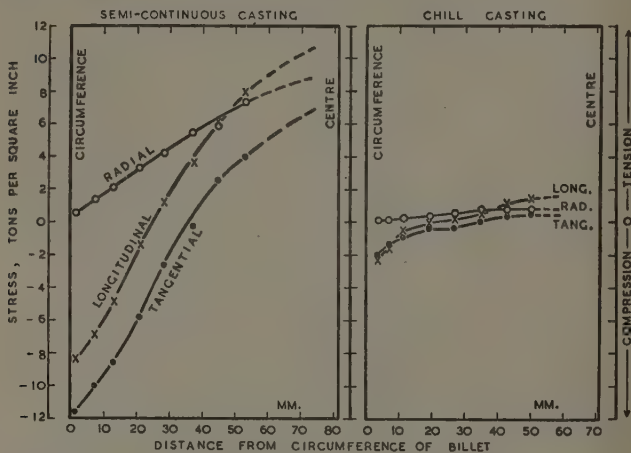


FIG. A.—Internal Stresses in Cylindrical Billet of Aluminium-Silicon Alloy.

Immediately the metal solidifies, it contracts away from the mould, and leaves a space into which inverse segregate can, and frequently does, exude. The blebbing, which may be irregular or banded, thus occurs over the whole length of the billet, unlike that in a chill casting, where it tends to be confined to the feeding head end. The surface layers, contracting against a central boss of hotter and intrinsically weaker material, are in tension: the stress may be relieved by plastic deformation or by the formation of hair cracks which may open up and give rise to trouble on subsequent fabrication. In extreme cases the stresses may be sufficiently great to cause the whole block to split. The possibility of trouble still exists when this stage has been passed, because in the later stages of cooling the central boss is contracting away from the cooler circumference. The latter is thus in compression and the centre in tension. Here again the magnitude of the stresses may be sufficient to cause cracking, and this time the cracking will be internal. Even if the block should survive the actual casting operation, there is no guarantee that it will not crack, say, on scalping or sawing to length. To give some idea of the magnitude and distribution of the stresses at this stage, I have plotted in Fig. A some figures obtained

by Roth and his colleagues * on an aluminium-13% silicon alloy billet. For this material the U.T.S. is of the order of 12-14 tons/in.²: it will be seen that the maximum stress imposed in casting does not fall far short of that figure. It is interesting to compare the stresses in a semi-continuously cast block with those in a chill casting of the same shape and nearly the same size: in the chill block they are negligible in comparison.

For producing a sound block by the semi-continuous process there is no royal road to success: for each particular alloy it is a matter of trial. The variables are: composition of the melt, temperature of the melt, length and breadth of the mould, casting speed, and amount and method of application of the cooling water. The conditions are often critical, and variation in one may involve changes in all the others.

One would rather expect that the rapid cooling through the solidification range would produce a fine structure, but this is not necessarily the case. There are two important stages in the solidification of an undercooled melt: the first that in which deposition occurs on pre-existing nuclei and crystal growth tends to be columnar, and the second, where new nuclei are formed and a mass of equi-axed crystals results; and the conditions of casting determine which of these two types will occur.

Fig. B (Plate CXXVI) shows the macrostructure of a block where columnar crystallization has not occurred, and the whole structure is fine: this was obtained with a low casting temperature and a medium speed of withdrawal. Fig. C (Plate CXXVI) represents a block in which cooling was slower, and columnar separation has had a chance to occur. The direction of the temperature gradients is shown by the manner of growth of the columnar crystals, while occasional arcs of equi-axed crystals show the position and shape of the solidification front.

Fig. D (Plate CXXVII) shows the effect of extremely rapid withdrawal, and very drastic cooling of the mould wall. The structure is almost that of a chill casting: the columnar crystals have grown inwards nearly horizontally and almost touch. The solidification front here is a deep pipe, not a dish, and conditions such as these can easily lead to bridging, with the possibility of gas entrapment. Fig. E (Plate CXXVII) shows a block in which the crystallization is almost entirely columnar, and nearly unidirectional. Under these conditions the grains can be extremely coarse. This type of structure is not desirable. Each of these crystals will deform more or less as a unit, and will recrystallize as a unit, so retaining something of its identity throughout even a long series of fabricating operations.

The microstructure of semi-continuously cast aluminium alloys is not very sensitive to the actual conditions of solidification: the particles of inter-metallic constituent are fine and uniformly distributed, as Fig. F (Plate CXXVIII) shows. The section was taken from a block of 1 $\frac{1}{4}$ %-manganese alloy, and the constituent visible is mostly MnAl₆.

Fig. G (Plate CXXVIII) shows the structure of a chill-cast block from the same melt. The particles are larger, and the matrix contains less manganese in solid solution. This has an important bearing on the behaviour of the alloy on subsequent fabrication: the U.T.S. of the continuously cast material will be slightly the higher, and its elongation slightly the lower, while there are pronounced differences in recrystallization, that of the continuously cast material being the more sluggish. Means are available for overcoming this difficulty, but the subject is outside the scope of this discussion. I only mention it now as an additional reason for stating that to change over from chill to semi-continuous casting is something not to be undertaken lightly and without due regard for its implications.

* A. Roth, M. Welsch, and H. Röhrig, *Aluminium*, 1942, 24, 206.

MR. F. C. EVANS * (Member): I would first congratulate the authors on the papers they have produced and the Institute on organizing this Symposium. Speaking as an ordinary member, I would like to say how much I appreciate this type of paper.

Passing on to particular papers, and taking the first one by Messrs. Bailey and Baker, I must congratulate them on the excellent summary they have provided of the many improvements which have been recently developed.

In this paper I notice that the authors remark themselves on the fact that pressure welding of cavities in non-ferrous metals appears to have received little attention. I have often wondered myself why this subject has not been investigated, as, while an obvious example of successful pressure welding of defects by the application of pressure and temperature is a rimming-steel ingot, as mentioned by the authors, the more obvious one for non-ferrous manufacturers is that of tough-pitch copper, as described in the paper by Waddington.

I am a little at a loss to understand why cavities in, for instance, phosphor-bronze ingots, which are due to unsoundness produced by the oxygen-hydrogen reaction, cannot be pressure-temperature welded, while similar cavities in copper can be. If the mechanism in pressure welding was more clearly understood, it might be possible, for instance, to produce, and work, ingots in high-shrinkage alloys such as aluminium bronze and manganese bronze with a controlled gas content, as they are in rimming steel and tough-pitch copper, and thereby avoid the very heavy discard which takes place in removing the shrinkage heads on these alloys. The average shrinkage head on an aluminium-bronze or manganese-bronze ingot is in the nature of 8-20%, according to the size of ingot, so that it will be realized that such a saving would be very considerable.

In another matter, I find a little discrepancy between the views expressed in different parts of the paper. This is with regard to the desirability of disturbing an alloy with extended freezing range, when dendrites have already formed in the mould while the higher-melting-point constituents are still liquid. On p. 300, the authors state:

"The first essential is to pour it at high temperature so that there is no tendency to premature solidification while the metal is in a disturbed condition."

Later, on p. 309, they say:

"It has been suggested, for example, that the pouring stream in top-poured ingots may detach small solid crystals from dendrites which have already formed in the mould and may disperse these through the remaining liquid and provide potential centres of crystallization which influence the macrostructure."

From my own experience, I would have thought that the second opinion was the one generally accepted, but I should be glad if the authors could expound on the difference between the two conflicting views. I am assuming they will be replying later.

Also in relation to this matter, I shall be glad of an opinion from the authors as to the use of supersonic or other vibrations for a similar purpose, that is, the breakdown of the dendrites to provide new centres of crystallization.

Much publicity of a not very informed kind was given to this matter some years ago, and I myself made a few crude experiments. I was unable, however, to observe any influence by supersonic or other vibrations on the macro-structure of various copper-base alloys.

* John Miles and Partners Ltd., London.

Passing to the paper by Messrs. Murphy and Callis, I was interested to read this very clear exposition of the principles and practice of the manufacture of aluminium-bronze billets by the Durville process.

I have myself been engaged in the manufacture of aluminium-bronze billets for hot-working purposes and was most interested to see how many of the rules laid down by the authors coincide with my own experience. They describe in their paper a Durville machine which is turned over by mechanical means, but I have also had experience of machines which cast by a manual process.

In this type of machine, the general arrangement is very much as shown in Fig. 2 of the paper, the only omission in the drawing being a trunnion at the top of the mould which supplies the axis of reversal. The whole apparatus must be carefully designed so that the mould and ladle, on either side of the axis, are counterbalanced, and so that even when the apparatus contains molten metal it can be turned from position 1 through positions 2, 3, 4, 5 to position 6 smoothly and effortlessly by manual means. This type of machine has the advantage that it allows the speed of tip to be varied at various angles without complicated mechanisms. The speed of tip is important. Generally speaking, when you are coming up to the horizontal you can take it at more or less any speed. It is when you are approaching the horizontal and are just crossing it that the operation is at its critical point. When the metal is flowing into the mould, you must take up a faster speed. This is rather difficult to reproduce by mechanical means, but it is quite easy to train an operator to do it. The other advantage of this type of machine is that it is cheap to manufacture and has no complicated mechanical or electrical mechanisms to maintain. It might be thought that the method is only suitable for small ingots, but with correct design, machines for casting ingots up to 300–400 lb. weight are successful.

A few remarks regarding the chill mould itself may be of interest. Initially, I used a design of chill mould which gave a tapered square billet, which is advantageous in theory. It was soon abandoned, however, as it was found almost impossible to obtain sound enough iron castings, defects always developing at the bottom of the mould cavity, presumably owing to blow-holes just below the skin. These cavities give difficulties in extracting the ingot from the mould and also lead to entangled oxides in the ingot due to "blowing" from the entrapped air. I changed the design, therefore, to a cylindrical cannon type of mould, closing the bottom with a cylindrical piece of copper some 5 or 6 in. in depth. This copper bottom helped with the directional cooling from the bottom which is so important in obtaining sound ingots. This method of construction also enabled renewal of the mould surface to be carried out by plain boring on a lathe.

In Section VIII on the control of composition, I notice that the authors draw special attention to the necessity for careful mixing in of the aluminium due to the large differences in densities between aluminium and the other constituents of the charge. Anyone who has manufactured aluminium bronze will know what a real difficulty this is.

I would like to draw attention, however, to the obvious solution to this problem, which is the use of a high-frequency induction furnace. Some years ago, I made a trial melt on a 250-lb. capacity, 2000-cycle high-frequency induction furnace. In this test, I first ran down the copper, nickel, and iron constituents of the charge. When this was molten and the iron properly dissolved, the aluminium ingot, which was 10% by weight of the charge, was placed on the top of the molten base charge. There was no plunging or manual mixing, and after three minutes, with the power on, the charge was poured into small ingots of about 10 lb. each. Careful analysis of the first and last ingot showed that the analyses were identical within the limits of error of method of analysis.

The problem of obtaining the aluminium perfectly distributed throughout the charge and the control of the aluminium content to a set figure are the main difficulties in the manufacture of aluminium bronze. This has always been so, but it is now of even greater importance as aluminium-bronze alloys are finding increasing application for compressor blades in axial-flow gas turbines. The manufacture of these blades by close stamping methods makes it essential that the aluminium content is held within at least $\pm 0.1\%$. Also methods of heat-treatment have been developed to produce the optimum mechanical properties for these blades for this service, and here again very close control of aluminium content is of paramount importance.

While the paper by Messrs. Bradbury and Turner is an excellent introduction to the method for modernizing a shop producing nickel-silver billets and great detail is gone into in some cases, I think that some more information on various points would be extremely helpful.

For instance, while some figures are given for the limit of impurities such as lead and sulphur, no figure at all is given for carbon. As has been pointed out in the paper by Bailey and Baker, the carbon content has a very important effect on the soundness of nickel-silver castings. This has been also my own experience and I am surprised to see, by implication anyway, that impurities are only controlled by the selection of scrap. I should be very glad to have the authors' views on the permissible quantities of carbon for the various compositions under discussion. In relation to carbon content, I should have thought the selection of silicon carbide crucibles was open to question as it is my experience that carbon is picked up more readily from silicon carbide crucibles than from graphite crucibles.

I was rather disappointed to find that after the very complete picture the authors have given of the financial and technical advantages of changing over from the old type of furnaces to the new arrangements that no comparative figures were given for melting losses. This applies also to Mr. Bond-Williams's paper. Nothing is said about the melting losses. With metal at the price it is to-day a small fluctuation in melting losses may have a very big effect on the financial success of a process, and some figures would have been very useful.

DR. N. P. ALLEN,* M.Met. (Member of Council): What I have to say may perhaps be out of place in this severely practical meeting, but if I may I would like to raise one or two general points.

In the first place, I would like to register a little grumble about the title of this Symposium. It is a Symposium not on the casting of non-ferrous metals but on the casting of copper alloys. That is not a criticism of the authors of the papers, but of the people who have experience of the casting of other metals but have not contributed. I hope that in due course they will remedy their omissions.

It is a pity, in a way, that the scope of the Symposium is not a little wider, because there is a great variety of properties in non-ferrous metals, and if we had considered the complete range of metals, some interesting generalizations might have come out. For example, if we consider the behaviour of the metals towards gases in relation to their position in the electrochemical series, we find that the noble metals, such as gold, platinum, and palladium, are metals in which troubles due to gaseous oxygen can arise, because their oxides are relatively unstable at high temperatures. When we come to copper, iron, nickel, cobalt, the oxides of which are stable, but not very stable, the troubles are principally due to the reaction of the oxide with some non-metallic impurity

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in the metal which has a gaseous oxide, such as hydrogen, carbon, and sulphur. In very base metals, such as aluminium and magnesium, the oxide is entirely stable and cannot be reduced by non-metallic impurities. In these cases gas porosity is almost entirely due to hydrogen.

The methods adopted for melting and casting are strongly influenced by this general relationship. Similarly, in the non-ferrous metals there is a great variety of melting points, and if the scope of the Symposium had been wider we might have been able to see how the difficulty of removing the latent heat affects the type of mould and the macrostructure produced.

The Symposium includes the methods used for copper and its alloys with zinc and aluminium and tin. In copper it is the reaction of oxygen with hydrogen and sulphur that matters. When tin is added tin oxide is formed, but the affinity of tin for oxygen is not so powerful that the melt cannot contain some dissolved oxygen. The dissolved oxygen can be used to limit the amount of hydrogen present. We therefore melt bronze in an oxidizing atmosphere. When aluminium is added to the alloy a very stable oxide is formed. The melt can contain no significant amount of oxygen, and there is nothing to prevent the hydrogen content rising to a high value. Consequently, when dealing with aluminium bronzes the general methods are much the same as in dealing with pure aluminium. That is, one has to guard against the entry of hydrogen and use the oxide skin on the molten metal as a barrier between the gas and the molten metal.

In copper-zinc alloys the metal is completely deoxidized by the zinc, but the vapour pressure of the zinc acts as a guard against entry of hydrogen.

There is also a very interesting series in connection with carbon. Where we have elements introduced into the melt which can combine with carbon the melt is apt to contain carbon, and the procedures adopted are such as to avoid the entry of carbon into the material. One can use graphite freely in dealing with copper, but not in dealing with nickel or copper-nickel alloy containing a high proportion of nickel.

We know a certain amount about these things, but our knowledge is not precise enough. One adds manganese to nickel silver to avoid unsoundness, the nickel-silver alloy being decidedly more sensitive to porosity than a simple brass. The proportion of zinc in the nickel silver is high, and its vapour pressure is high, so that high hydrogen contents are unlikely. The alloy should be completely deoxidized, so that severe porosity would hardly be expected. Yet porosity is encountered, and manganese does something to improve matters; but just what the manganese is doing, whether it is, for example, rendering innocuous some carbon or sulphur in the melt, or whether it acts in some other way, is something that I think nobody can answer clearly.

That brings me to the point that we need to study more fully the chemistry of molten metal. In the case of copper alloys the unsoundness of the casting is the thing which has to be controlled, but in the case of other alloys, such as aluminium and magnesium, the chemistry we need is the chemistry of the production of small particles such as may act as nuclei for crystallization. These no doubt affect the mode of crystallization in a very profound way and lead to the difficulties to which Mr. Phillips made reference.

While emphasizing the importance of the detailed knowledge of the chemistry of the molten metal, I would like to make reference to the paper by Waddington, which is such an interesting example of a logically designed metallurgical process. The process was possible principally because there was, when the plant was being laid out, a fairly clear knowledge of the controlling factors in producing the porosity of copper. It was known that sulphur and hydrogen were the things to be guarded against. It was found possible to get rid of the sulphur by studying the anode and getting conditions such that the structure of the anode did not cause the electrolyte to be entangled.

Hydrogen was got away by heating in an atmosphere composed of nitrogen and carbon monoxide and arranging for a flow of the atmosphere through the furnace. The oxygen content was controlled in such a way as to make sure that such hydrogen as did remain was kept at a low value. The knowledge that such gas as was evolved came off in the last stage of solidification made it reasonable to attach importance to the speed of solidification and resulted in the introduction of the water-cooled casting and the close control of the structure of the ingot. The detailed knowledge of the operation and the will to control in detail is really the secret of the success of that very remarkable and smoothly working plant.

DR. R. GENDERS,* M.B.E. (Member): I do not want to criticize in any detail any of the papers. They cover a very wide scope, and the gaps are being usefully filled in by the discussion. I want particularly to extend that process by adding some remarks on another aspect of metal casting and fabrication which is interesting and has not perhaps received the attention it deserves.

I refer to the practice of using for fabrication purposes cast metal which has been worked very little if at all before being used for machining or cold working. A case of that kind is the casting of small slugs of brass which are then heated up and immediately used for hot-stamping purposes, or cups may be made from them and these cups may then be further cold worked without having recourse to the rolling and annealing involved in the production of sheet.

There are some advantages in the use of a cast slug, because if it is sound and the structure is uniform, equi-axed, it is very suitable indeed for forging, having no "grain" and being thus largely immune from defects if there are upsetting movements in the metal during the forging process. There are also indications—which are as yet fairly new and not fully investigated—that when the cast structure is cold worked it is less liable to season-cracking than a structure which has been recrystallized and worked time and time again. I was very interested, therefore, to have an opportunity recently to study on the Continent a process which gives a material of this kind and in a much better and cheaper form than single cast slugs, the production of which by sand casting has obvious drawbacks. This process, which is known as the "Soro" process, has some fascinating features. It consists in the centrifugal casting of a ring, one metre in diameter, having the section of the bar required. The inner edge of the ring is shaped on a horizontal lathe to remove the "feeding head", and the ring is then cut and straightened out to form a bar, which is put through a scalping machine, giving finally a straight bar 10 ft. long. Being centrifugally cast, the material is very fine in structure, and free from slag and other non-metallic inclusions. It can be either drawn and used for machining or cut into lengths for forging. Most materials, including bearing bronzes and so on, have been cast by the method. The original plant is understood to be producing one thousand tons a year. The molten alloy is poured down a spout leading into a revolving ring-shaped divided mould, and the cast ring, resembling a thick hoop, is extracted quite conveniently when the mould is parted. Rings are produced in sectional diameters from 10 mm. up to 80 mm. Such a process appears useful for providing cast material of high quality in bar form in a variety of sizes.

As regards the papers in this Symposium, it would be rather surprising if I had any criticism to make of that by Bailey and Baker. Bailey and I worked so long and so agreeably together in this field that I am sure there is nothing in the paper which I should not say myself. I would like to congratulate the authors on producing such a splendid condensation of the known effects of

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the main variables of the casting process. I am sure that it will be a useful means of reference for many years.

The contribution by Murphy and Callis is to be welcomed as one of the few papers showing how progressive workers in this country have developed the use of the Durville process and secured something of its value. It might suitably be recorded that the Durville process was first of all noticed and introduced into this country by Dr. R. S. Hutton, then Director of the British Non-Ferrous Metals Research Association. It had been used in France to deal with the difficulties of casting material for the aluminium-bronze French coinage. I well remember the first expedition to see the Durville process at Mouy-Bury, where Durville had built his foundry in the grounds of his residence and staffed it entirely by agricultural workers. We were much impressed to see this remarkable plant producing beautiful golden smooth ingots of aluminium bronze greatly superior to the crucible-cast product commonly used at that time.

Finally, I would like to congratulate the Institute on this collection of papers and hope that the habit of the Institute of holding such Symposiums may be continued.

DR. GEORGES BLANC* (Member): We always read your papers with the utmost interest, and I am pleased to say that our practice in France confirms many of your views.

The oxidizing atmosphere has been adopted by the leading French foundries, but there is some resistance due to the somewhat higher consumption of crucibles. Of course, people are beginning to understand that if they reduce the number of heats of each crucible by 15% and raise the yield in sound metal by 10% the balance sheet is still in their favour.

If we consider the oxidizing flame as a sound hygienic practice, I would compare the use of oxidizing fluxes to a medical cure and recommend it preferably in homœopathic doses. But the use of processes like scavenging with dry nitrogen appears to me to be a little like surgery, and we recommend it only when such adverse conditions are present simultaneously that other means will not do. We might sometimes consider it as a remedy for the lack of sound workmanship, but in such cases it must be only a temporary way of preventing big troubles.

We have recently had an opportunity of making systematic experiments in the use of nitrogen treatment for high-lead tin bronze, half the melt being poured without treatment and the other half with five minutes of energetic bubbling, in each case with and without deoxidation, by means of phosphor copper. With nitrogen treatment and deoxidation we had 100% sound pieces in series over which the foundry had experienced a good deal of trouble. The tensile test, on the sound bars only, gave us an average of 20% tensile strength higher. For this alloy, which had about 15% lead and 5% tin, we had about 13 tons/in.² instead of 11 on the best of the untreated bars. These figures may seem somewhat low, but the experiments were made in an ordinary industrial foundry and not in an experimental one.

The elongation had also risen from 10 to 13% on a length of 3 in. Our bars are a little longer than yours. The strange thing was that the reduction in area was more than twice as large. The ratio of the reduction in area to the elongation rose from 1.1 to 1.5 or 1.6. Another interesting thing which we observed is this. We used for our test bars a clover-leaf section, rather like a cross, and compared the tensile strength in the arms and in the centre. When the bars were not treated, there was not much difference between the centre and the arms. When they were treated, we had a difference of about 20% less

* Director of Research, Centre Technique des Industries de la Fonderie, Paris.

in the centre than in the arms, and we attribute it to a shrinkage effect. We think there would be some danger of replacing gas troubles with shrinkage troubles.

I am afraid that, as far as industrial practice is concerned, I cannot agree with Mr. Baker's conclusion, partially to re-gas the metal in order to avoid these shrinkage troubles, because I think it requires too much precision for an industrial foundry. It might be possible in a small crucible, but in the normal furnace it would be difficult to re-gas and get a good structure for the metal. The solution must be found rather in the design of the moulds or in the use of chills or in the rate of pouring. I do not think the rate of pouring has been studied sufficiently, and there is here a large field for research.

To come back to the nitrogen treatment, we observed that it worked exactly as an oxidizing process. And I wonder whether it did not work more by mixing the metal than by proper scavenging. We bubbled it five minutes, and very energetically, so that every part of the bath could come to the surface, and we did not stop the heating. It was all done in an oxidizing atmosphere. In such conditions our workmen would not like to mix the bath or they would slow down the flame and sometimes produce a reducing atmosphere over the bath. What we tried to do—I have not received the results yet: it is too recent—was to make a device to mix the bath in the crucible without suppressing the flame and continuing to use the oxidizing flame.

All these studies are, I think, very interesting, and I am very pleased to be able to work on parallel lines with research in Britain.

M. LOISEAU *: My company has used since its foundation the tilting process to cast not only aluminium bronze but also high-resistance bronzes and brasses containing aluminium, and even, exceptionally, other alloys free of aluminium. In the casting of ingots the process always gives excellent products provided that, as Messrs. Murphy and Callis point out, the ingots are not too long compared with their section. If the ingots are too long in comparison with their transverse dimensions, some "bridging" can occur during their solidification, and, as a result, unsoundness may appear in the central zone. A longitudinal section of the ingot shows, after polishing, zones of micro-shrinkage alternating with sound zones. Increasing the volume of the feeding head or reheating it is of no help in such cases. The ratio of 8 : 1 indicated by the authors seems to be a maximum. In current practice it is advisable to keep it under 6 : 1.

The soundness of the ingots also depends on the taper; tapered ingots are generally sounder and can be used without difficulty for forging or rolling. Tilting can be used also for sand castings, but it is necessary to guard against the danger of the cores being displaced or deformed. Excellent results have been obtained with gun-metal or tin-bronze castings.

DR. BLANC: I should like to add to M. Loiseau's statement that the tilting process necessitates a certain "know how". The Centre Technique des Industries de la Fonderie has compared the characteristics of test bars machined from ingots of various forms, cast in sand by various processes. The highest tensile strengths, which corresponded to the largest elongations and to the smallest dispersion of results, have been obtained with test bars machined out of clover-leaf-section ingots that were poured by tilting in M. Loiseau's foundry, where it is the common practice. Values with top-poured ingots were somewhat lower, and identical to those obtained from another foundry's similar ingots poured in the same way. But this other foundry's tilted ingots were not so good as its top-poured ingots and gave more dispersion of results.†

* President, Le Bronze Industriel, R. Loiseau & Cie., Bobigny, France.

† *Fonderie*, 1947, (19), 721.

Dr. Genders made an allusion to the visit paid to the little foundry in Mouy-Bury by the members of the British Non-Ferrous Metals Research Association some 22 years ago when this Association secured for its members the rights on M. Durville's British Patent. At that time, the validity of this patent was already very near to its end, and we highly appreciated the fair play of the British Association in their dealing with our company. I had the honour and the pleasure of welcoming the Association's members and of showing them all particulars about our routine practice in carrying out the process, which has suffered practically no alteration since that time, but is used on a much larger scale. I am pleased to realize that our co-operation on this occasion as well as on many others has been fruitful.

MR. J. O. HITCHCOCK,* B.Sc. (Member): Messrs. Bailey and Baker say at the top of p. 303:

"An important, and in some cases over-ruling, consideration is the desirability of casting large ingots, even though the final product may be required in short lengths."

Perhaps there is the implied suggestion here that large ingots are not generally desirable, whereas for the production of standardized sizes, sheet and strip, for example, it is generally true that the larger the ingot the higher the ratio of saleable metal to cast weight. This statement by Bailey and Baker does suggest that this problem is being regarded too much from the point of view of what is the best shape and form of ingot to give sound ingots of good surface, whereas from the technological aspect one should perhaps study the best melting and casting technique to make metallurgically satisfactory ingots of the size and shape most suitable for subsequent processing on available equipment, particularly bearing in mind the economics of different sizes of ingots in relation to the percentage yield of what Cook and Fletcher refer to as "marketable material".

In fact, the merit of a particular casting technique should perhaps be judged largely on this basis, since in the majority of cases it can fairly readily be shown that attention to perfecting the casting process to avoid feeding-head waste, swarf, and other scrap is very well repaid by the consequent increased yield of final product. It is, in fact, frequently surprising on examination of some casting processes, to find how a simple modification to the geometry of the ingots can give an increased yield without changing the casting technique in any way.

I should like to ask the authors if they can give us some indication of the final yield of marketable material they get for certain specific products.

It is consideration of this question of yield which focuses attention on the continuous casting methods referred to in the various papers, since by such processes the yield should be substantially higher than by the present standard methods.

The Durville method mentioned and described is also attractive from this point of view, but it suffers from dimensional limitations such as we have just heard from our French friends. This, surely, is in the nature of a challenge to metallurgists, since if one could overcome the piping effect when the ratio of length and diameter is greater than 8:1, there would surely be great advantages to be obtained.

A simple practice which might be of use is to keep the feeding head of the ingot molten after casting by striking an electric arc, perhaps through a slag, for such time as is necessary to secure adequate feeding. This can be done very simply, and it has already been found practically effective in reducing

* Henry Wiggin and Co. Ltd., Birmingham.

discard. Alternatively, there are other methods of keeping a feeding head molten, for example by using an electrical-resistance-heated hot top. I am sure such methods would be cheaper in the long run than resorting to static casting of round billets, with the subsequent loss of metal due to the necessity of machining the surface, as described in the paper by Murphy and Callis. It would be interesting to hear what experimental work has been carried out in this direction.

MR. G. SKRIFT * (Member) : An old and a new method have been discussed to-day. I saw *Punch* this week, and there was a shop assistant who asked a lady who came in whether she would like to have an old look but not the one which preceded the new look. I think that applies here also, and I would like to discuss the old method, but not the one which preceded the new method.

As far as melting is concerned, nothing has been said in the Symposium about rotary furnaces. We have had experience with rotary furnaces, particularly for gun-metal and brasses, and find they give excellent results. First of all, you can achieve a better slag-metal reaction and all the oxidation processes can be better conducted. Also they reduce melting losses if used properly.

We have achieved results, measured over a period of a week, of 0.37% loss with melting gun-metal—and scrap gun-metal at that. (Metal thus produced can be hot worked.) Even tin bronzes and nickel silvers can be hot rolled if proper oxidation treatment is used.

I would rather like to state, with Professor O'Neill, that there is some idiosyncrasy as to thermodynamics in the Symposium, and I am sorry to see that no one to-day has ventured to say anything about it. I hope that will be corrected this afternoon.

I was sorry also that in the Symposium the name was not mentioned of Dr. Lepp, who carried out oxidizing processes as early as the beginning of the thirties. Talking about the Durville process and the melting of aluminium bronzes, we used this process extensively in casting billets up to half a ton. While for smaller billets, as Mr. Evans said, up to 400 lb., a hand machine can be used, for larger billets you require mechanically operated machines. Such a machine was designed by us, and we paid particular attention to not having a jerk when the centre of gravity becomes shifted from one side of the machine to another. That is a very important point which was frequently overlooked. I remember during the war we had some mechanically operated machines installed by an unlucky firm which was bombed out, and we had to produce the billets for periscope tubes. We had constant difficulties at this stage when the machines tipped from one side to the other.

I would like to say something about the melting of aluminium bronze. It is still very frequently melted in coke- and oil-fired furnaces. I saw a very wide use of electric furnaces in the States. I visited various foundries a few years ago, and I saw rocking-arc furnaces used largely for aluminium-bronze castings, aluminium-bronze billets, and sand castings.

The discussion I had with the heads of the firms confirmed that these furnaces are very suitable for aluminium bronze. They produce very good and very uniform material.

I saw also a high-frequency furnace used for aluminium bronze, and that, of course, is a very good way of melting aluminium bronze, particularly when alloyed from virgin materials, as mentioned by Mr. Evans to-day. But it is not out of the question that aluminium bronzes could be melted in a rotary furnace, particularly the alloys where very high tensile strengths are not required. A lot of them are still being used for the chemical industry and not

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for turbine blades, &c., where just simple static tensile strengths are required. There is a definite possibility of using a rotary furnace for these purposes. There are difficulties and complications. Fluxes which will be required are poisonous by nature and excellent extraction is essential.

Generally speaking, I would like to congratulate the authors and the Institute of Metals on the papers. This is, I think, the first real attempt to bring the science and the industry closer together.

PROFESSOR F. C. THOMPSON,* D.Met., M.Sc. (Member of Council): The ordinary curve for the strength of a casting as a function of temperature shows a maximum falling away both at lower and higher casting temperatures. The low strength at low casting temperatures is explicable on the grounds of cold lapping, and at high temperatures as a result of columnar crystallization. It is well known that one can simulate practically all the defects in an ingot or a casting in a suitable stearine wax, and when the corresponding curve is obtained for such a wax, at still higher casting temperatures the curve again rises. That has been found so often there can be no doubt about it. The very high-temperature casting is completely columnar from the surface to the centre. Has anything corresponding with this increase of strength at these excessively high casting temperatures ever been obtained in a metal?

One other point which has always given me a great deal of difficulty is the quite sudden change from the external columnar crystallization to the internal equi-axed. Attempts have been made to explain that in a number of directions, none of them, I think, very satisfactorily, and any adequate explanation of that quite sudden change of macrostructure would be extremely interesting.

MR. G. T. CALLIS,† B.Sc. (Tech.) (Member): Some amplification would seem to be desirable of the statements made on pp. 335 and 337 in connection with the significance of the ratio of length to diameter of ingots made by the Durville casting process and with the use of hardness testing as a check on composition. A very slow speed of rotation of the table of the machine over the horizontal is essential if the characteristic perfection of surface of the ingots is to be realized; during this period freezing of the liquid metal from the submerged lower side of the mould can occur while the last of the metal is still entering from the container. This early solidification naturally takes place more readily towards the bottom end of the ingot mould, resulting in a tendency to bridging and to a more or less central zone of shrinkage unsoundness at the end of the ingot remote from the head. This internal unsoundness does not become a serious problem unless the ratio of length to diameter exceeds 6:1, although ingots whose length is 8 times the diameter are satisfactorily used directly for the manufacture of drop-stamped rings, for example, in which any trace of central porosity in the "use", struck axially in the dies, can be kept within the bounds of the metal removed from the centre as the clipping.

The production of ingots by the Durville process lends itself to a lay-out on semi-mechanized lines, and the speed of production from say four machines can be so high that a large number of individual melts are made per day. The plant, of which one unit is illustrated in Fig. 5, was capable of producing aluminium-bronze ingots at the rate of some 200 per day, and the satisfaction of the specifications governing the final wrought products necessitated a close control of the aluminium content. Chemical analysis of every melt was impracticable as a day-to-day method of control, but it was found that the Brinell hardness of the ingots could be correlated reliably with the aluminium content. The test was adequately sensitive, and with a mechanically-operated

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† Formerly Metallurgist, J. Stone & Co. Ltd., London; now Chief Metallurgist, Manganese Bronze and Brass Co. Ltd., Birkenhead.

direct-reading Brinell machine, the operation could be carried out expeditiously with simple mechanical handling devices.

MR. N. I. BOND-WILLIAMS,* B.Sc. (Member): I have one or two points which I think might add provocation to the discussion, and which in fairness I would not have expected Professor O'Neill to include in his introductory remarks.

When I was asked to produce a paper of this kind, I had in mind at the time and I believe it still exists that there is a good deal of criticism of British industry for its failure to take advantage of the results of scientific research. In fact, I could quote from the *Economist* which said in one of its publications that: "Spread over the whole range of British industry the volume of genuine scientific research is very thin. Moreover, apart from fundamental research there is a lack of willingness to find the time or expend the money for proper development, although long and extensive development is essential, at every stage of which the scientist and the production expert must stand side by side. That is what is chiefly lacking in British industry."

I had that in mind, and in preparing this paper I was particularly careful, as far as I could be, to illustrate the simplicity of a particular individual application of the results of research; the fact that it could be done without the tremendous expense suggested in my quotation, and by quite a small industrial unit. We have to remember that the majority of industrial units in this country are small; that they have not the large facilities available to those few of our bigger brethren. In presenting this paper, I was particularly careful to avoid anything which would frighten off that particular class of industrialist. In particular, I avoided thermodynamics for that very reason. I will admit here that personally I have had discussions with scientists on thermodynamics who professed to understand them, whereas I have little more than the jargon of it at my command, but I managed to survive. The complication of thermodynamics is such that I do not think that the small industrialists would have understood a word of what was going on, so I was careful not to frighten them by reference to anything more than was necessary to illustrate the application of the published work. In the same way, the chemical and physical-chemical arguments on flux degassing were carefully avoided.

Again, you will notice in this paper that there is rather a remarkable absence of numerical data and information. That, too, was deliberate, because the result of the degassing process is calculated, among other things, to produce rather interesting increases in physical properties. To quote these, in a paper illustrating an application for purely commercial uses, would be to fog the issue and to indicate that the object of the work was not to improve the technique for an existing product but to improve a product. That was not the impression that I wished to convey, although incidentally that was an actual result.

The other feature, of course, is that figures or any numerical data, taken from works practice, are liable to fluctuate to quite a considerable extent. There is also a danger that the methods of recording information from factory to factory would be different, and that over a period of time variables not covered by the paper might occur which would provide ammunition for the destruction of any figures that I might quote. As a matter of fact, that has already happened, in the discussion, in the matter of consumption of coke per ton. I can assure Mr. Molineux that that figure has actually been attained. Otherwise I would not have quoted it. But it is the sort of thing which I will agree is not really open to debate as to its validity owing to very different local conditions.

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I would like to emphasize that in encouraging a general discussion of this kind on the application of scientific research in a small factory I am not attempting to conceal these figures, and if any figures that I have are of value to members or to organizations, I should be very pleased to provide them. But I do not regard them as sufficiently substantive figures to be published by such a body as the Institute of Metals.

MR. H. W. G. HIGNETT,* B.Sc. (Member of Council): As I have been called upon on the spur of the moment, I have only one point to make, and that is to emphasize the complication of casting alloys. As Mr. Molineux emphasized the human element it is perhaps a good thing that that complication should be emphasized.

There are two ways of looking at the problem of the human element. One way, which applies to the smaller unit, is to teach everyone involved in the casting operation that he is performing a most complicated and most useful task. And as Mr. Molineux suggested, it is a task that ought to be well paid for. On the other hand, in the larger unit the human element could be looked after by eliminating it to the maximum extent, and therein comes the use of these modern processes such as continuous casting. Their real value is that they are complicated processes requiring meticulous attention to every small detail in their control. If any small detail goes wrong, the effects are disastrous, and that, I suggest, is in their favour. The very fact that the effects of anything going wrong are so disastrous means that the people controlling the process have to keep on their toes. Therefore we have on the one hand a series of fairly simple operations magnified in application and importance; on the other hand an elaborate piece of apparatus requiring the very careful attention to detail of everybody concerned. In these two ways we can perhaps overcome most of the difficulties involved in producing a sound casting, or as I think Mr. Davies suggested, the soundest obtainable.

DR. L. NORTHCOTT † (Member): Before dealing with the individual papers, I would like to raise a point relating to an aspect of procedure which is dealt with in many of them. I refer to the casting operation and to mould dressings in particular. Although the different alloys may be expected to require rather different treatments as far as mould dressings are concerned, only one material—Mr. Waddington's copper—is limited to bone ash without any oily material, and it is fairly clear from the results he gives of analysis of the castings that the oxygen contained in his ingots goes up by an appreciable amount. In the case of copper, that does not matter, because a finished oxide or oxygen content is required in the ingot. In other cases, a flaming dressing is used with something like bone ash, graphite, or some solid material of that kind. I think the term "flaming dressing" is an extremely good one, whichever way you look at it! It seems to me rather amazing, in this year of 1949, that flaming dressings are still used. In the investigations carried out for the British Non-Ferrous Research Association at Woolwich a quarter of a century ago, largely by Mr. Bailey (I had the pleasure of assisting him in some minor capacity in those days), very definite evidence was shown that the flaming dressing did give rise to sub-surface cavities which led to spills and other defects when the material was worked. Bailey developed a technique of using a soot dressing with an externally applied reducing atmosphere. Very excellent castings were obtained, free from any sign of sub-surface on the spills.

Coming to the papers, first of all the one by Bradbury and Turner, I have

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† Superintendent, Metallurgical Branch, Armament Research Establishment, Woolwich.

been in some difficulty here in deciding whether the authors have made a very bad case for a modernized outfit, or a very good case for one which needs modernizing. The two principal modifications which have been introduced over the last half century have been on the one hand the introduction of oil-fired furnaces instead of coke furnaces and on the other hand the introduction of the water-cooled copper mould in place of the original cast iron mould. I think the authors would do both themselves and their firm greater justice if they gave some factual data as to the types of materials—the obviously very wide range of materials—which they have to make, but in the two instances—the mould and the furnace—they seem to be sitting on the fence. They are undecided whether to go right over to an oil-fired furnace, since in fact they have twice as many coke-fired as they have oil-fired. So they do not seem to be satisfied that oil-fired furnaces are better than coke-fired. Nor have they gone right over to water-cooled copper moulds, so I think there is an obvious reason for this, but I cannot see what it is. I would remind the authors that I have read their paper several times so I think they will not quote the sometimes justified retort that the paper should be re-read.

Coming to the paper by Murphy and Callis on aluminium bronze, I have just time to show a slide emphasizing the point they may be aware of—the use of the Durville technique for casting at extremely low casting temperatures [slide shown]. The two figures show, at the top, the coarse structure of a steel ingot cast by normal methods. The lower figure shows the fine structure of a Durville casting from the same melt, but cast at a very low temperature. You will see the difference between the macrostructures in these two ingots. I will emphasize that the Durville casting gives easily a far superior surface over any other type of casting I have ever come across.

There is one minor point: I might just have time to have a mild disagreement with Messrs. Murphy and Callis on their reference on p. 328 to the “surface tension” of the oxide film. I would like to ask what they consider to be the “surface tension” of a solid film of aluminium oxide.

PROFESSOR H. O'NEILL (*Rapporteur*) summarized the morning's discussion. He said: My task is to assist the transition from this morning's deliberations to those of this afternoon. It struck me this morning that there was now a very general appreciation on the part of those who have to produce cast metal of the work that has been done by researchers and the Research Associations. I formed the impression that industry now turns very naturally to its appropriate Research Association to obtain advice about any trouble that may have arisen or to seek help to enable developments to be made. That promises well for the future, as all technical improvements should be a great advantage to the country.

Dr. Allen suggested some generalizations which come under this heading of research. He referred to the paper by Mr. Waddington, which has been received with such general approval, and pointed out that probably it was possible for this fine plant to be built because the theory of gas reactions in molten copper was well understood. If we had the reactions for various alloys worked out in the same way, it might be straightforward to design plants which would perform with precision, just as the one at Copper Cliff appears to do. I think it was a very helpful point which Dr. Allen made. He also suggested a generalization on the position of metals in the Periodic Table and their reactions with gases. The noble metals get trouble with oxygen because their oxides are unstable, while the base metals at the other end of the Table suffer from troubles with hydrogen. That is an idea which may be worthy of further attention.

A plea was made for more thermodynamics, and it was mentioned that there had been no reference to the work of Dr. Lepp. Regret was expressed

that the papers in the Symposium dealt almost exclusively with copper alloys. If the discussion this afternoon could record more facts and observations about aluminium and other alloys, it would apparently be appreciated by most members present.

Several speakers emphasized the difficulties and complexities of the casting process as a whole. The opener of the discussion had thought out thirty possible casting troubles, all of which he believed could be overcome; but he emphasized just how difficult it was to get everything right. Other speakers referred to the human element in making castings and said that the workman should be encouraged to realize what a serious and valuable job his was. There was a difference of opinion as to whether the aim should be to get all the processes highly mechanized, or whether it was necessary, human beings being human persons, to have procedures whereby they could flourish their skill and exercise those human qualities which we know so well.

Then, a great deal was said about tranquil casting and that which is not so tranquil. I was impressed by the figures given by Mr. Phillips for the values of internal stress in semi-continuous cast slabs. It would be interesting to hear whether these stresses produce trouble of a serious nature in technical practice. When Mr. Phillips showed that some of the slabs had internal stresses approaching the nominal tensile strength of the alloy, one appreciated his warning against embarking upon continuous casting processes in a light-hearted spirit.

I think my last remarks should deal with mould washes. It has been said that the papers do not contain a great deal about them, and even that is not very scientific. It seems that members would welcome more discussion and information about the way in which mould washes operate, and the subject requires to be put on a more scientific footing. One speaker spoke of "flaming" mould washes as being a real description of what some of them are. If we could have more information about what is behind the behaviour of these different mould dressings, it would be an advantage.

MR. W. F. BRAZENER * (Member): It could not be expected in only one day to cover more ground than has been covered so well by the authors whose papers are before us. A number of important processes and developments have of necessity only been touched upon in brief fashion. Nevertheless, the picture drawn covers a very large part of copper and copper-rich alloy casting as it is carried out to-day. This Symposium within its scope may in fact be regarded as the display cabinet of 1949, and in a generation's time can be referred to in order to see what definite advances will have been made in that future period. Those of us whose experience extends over a generation or more in this field will know at first hand of the improvements that have been made. There has been a combination of fundamental knowledge and electrical and mechanical developments which has tended to create a reasonable assurance of sound castings instead of the uncertain quality obtained from our old-world rule-of-thumb and hit-and-miss practices.

Although there is still a large production of ingots from open flat-type moulds, vertical moulds of the cannon or box type are becoming increasingly used. Metal with a high rate of shrinkage cannot, unless special precautions are taken, be successfully cast into open moulds. Tough-pitch copper is eminently suitable, as the oxygen content of the copper can be controlled to produce a level set on solidification. 60:40 brass is also suitable, provided that the pouring temperature is not too high. The best zinc slabs cast in open moulds are, after pouring, surface heated with an electric heater in order to keep the surface molten and maintain a steady rate of solidification from the

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bottom. Unless this is done, there is a tendency for shrinkage to cause a break in the surface and render the ingot unsuitable for rolling. Deoxidized copper and alpha-brasses are examples of metals which cannot be cast successfully in open moulds.

The modern development of continuous casting is a further illustration of the successful application of vertical pouring, which one may assume is preferable wherever it can be applied for sound ingot production.

In the casting of non-ferrous alloys for further working, probably the greatest step in recent years has been the introduction of the water-cooled mould with vertical pouring. Water cooling is a very old practice. In 1926, your President was mainly instrumental in introducing into this country the larger Junker type of water-cooled moulds for use with the Ajax-Wyatt low-frequency electric melting furnaces. It was my good fortune to carry out the initial experimental work. Many valuable lessons were learned in those early days.

Cook and Fletcher refer to the high cost of this type of mould. I would agree that the initial cost is high as compared with the cast-iron book-type or cannon mould. But, as indicated by Bradbury and Turner in their description of nickel-silver casting, there is no comparison between these two types in length of life. In cost per ton of metal cast, the copper-faced water-cooled mould is by far the cheaper. Furthermore, the mould surface retains its soundness for an almost indefinite period, whereas the cast iron soon starts to develop cracks, with their consequent disadvantages.

The backs of the Junker moulds were originally sectionally constructed. The best results are obtained by machining the back from the solid (usually a rolled copper slab). Also, with a little ingenuity, the retaining bolts can be so positioned that in no circumstances, other than complete fracture, can water leak into the mould. Another advantage is to substitute for fibrous packing of the mould joints machined metal-to-metal joints, to make the water-seal.

Both Bailey and Baker and Cook and Fletcher refer to grain refinement by using a flaming mould dressing. I should like to have their views as to the reason for this. The non-flaming dressing usually leaves a deposit on the mould face, and this could act to some extent as an insulator, retarding the transfer of heat from the ingot to the mould. Is this thermal effect sufficient to cause the marked difference in structure of ingots cast with these two types of dressing? Or is it possible that finely divided products of combustion from the flaming dressing become entrapped in the metal stream and form nuclei for crystal formation? A large grain structure can cause failure of an ingot in either subsequent hot or cold rolling, and this question of grain refinement is of considerable importance.

Waddington's paper on the production of tough-pitch copper shapes describes a process which is a model of progressive development. It is doubtful whether any copper refiner of thirty or forty years ago could have visualized continuous charging, refining, and pouring of such a fickle and temperamental metal as tough-pitch copper was thought to be. If the latest developments of mechanically controlled continuous casting replace the casting wheel, I wonder, with the knowledge now at our disposal, how many metallurgical specialists in this branch of our industry can see much further progress in the casting of tough-pitch copper shapes.

It is perhaps of interest to note the careful inspection of the cathodes before being charged into the furnace. One sees here that many of the headaches of the reverberatory furnace refinery have been transferred to the electro refinery. I have no doubt that commercially it has been well worth-while. At all events, as far as the finish of the resulting ingots is concerned, many here can testify to their soundness and uniformity.

One question will inevitably come to mind as a result of this development

in copper refining. Can the makers of Bessemerized copper produce Bessemer bar to such a degree of purity that the method of final refining for casting into shapes may follow the continuous process at Copper Cliff? Some brands of Bessemer bar produced to-day are of a high standard of purity, and in spite of what we may now believe to be insuperable difficulties, it may be well worthwhile to strive for a quality which can be used in a continuous refining process.

While on the subject of the casting of copper—and one might almost include phosphor bronze—it is very appropriate to recall the work carried out by Allen and his collaborators on the effect of dissolved hydrogen in molten copper. Reference is made in certain of the papers to the work that was carried out, and it is true to say that since the results were made public, the reasons for porosity in copper—and what is even more important, the steps to be taken to avoid this porosity—have been more readily understood. Bond-Williams, in his paper on the flux degassing of phosphor bronze, demonstrates in a practical way the application of Allen's experiments; one of his essentials for a sound chill-cast phosphor-bronze ingot being the removal of dissolved gases by increase in oxygen content. Waddington also mentions, in his reference to the technical control of the melting process of copper, the essentiality of a controlled oxygen content of the furnace atmosphere, sufficient to produce an oxygen content in the metal bath of about 0.010%. There are probably many instances of ingot porosity which could be explained and remedied by more detailed references to these papers on hydrogen in copper and the reaction between steam and molten copper.

I noted with interest references both by Bond-Williams and Bradbury and Turner to the Wigley type of crucible furnace; and I say this in spite of what Mr. Molineux said this morning. Trials which I carried out nearly thirty years ago showed considerable fuel and labour saving, as compared with the old haphazard air-intake variety. This development had a dual beneficial effect. The management reduced its costs by a lower expenditure on coke, while the operative earned his coppers (or should one say his brass) with less labour effort. In my experience, a casting gang on Wigley furnaces, doing four or five rounds per day, would finish at least an hour before a gang on similar work using furnaces of the old type. Since human fatigue plays its part in the quality of crucible cast ingots, anything done to lessen operative effort is a metallurgical advance.

MR. E. A. BOLTON,* M.Sc. (Member of Council): It is somewhat difficult for a speaker entering the discussion in the afternoon to find new points, and it was very disconcerting to sit through the morning session and to hear the points one had in mind being taken up one by one.

I should like to say a little on the subject of very large castings. I am thinking of castings of the order of one, two, three, or even more tons which are destined for rolling into plate. In many cases the rolled plate is for use in condensers, chemical plant, and so on, and the great essential is that it should be free from porosity under hydraulic test. Mr. Brazener referred to the method of casting in open moulds and, I think quite rightly, said that the method is going out of use; but it is still in great use for some of these large castings and, as he said, for alloys of the 60 : 40 brass type it is still eminently suitable. It is not so suitable for some of the other alloys, such as the aluminium bronzes, where shrinkage is inclined to play a more important part.

Quite recently I had occasion to make a number of castings of the order of about 35 cwt. each for rolling into plate, and at first sight it seemed desirable to make these in open moulds in order to avoid the feeding difficulties which

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occur with upright castings and the heavy discard which takes place from such castings in the form of a gate end.

Every effort was made to get unidirectional solidification by using heavy copper bottoms which, in some cases, were water cooled. The sides of the mould, which are formed of a cast iron ring, were heavily insulated with a thick bone-ash coating. The open top was kept as hot as possible by layers of charcoal, partly burnt, and incandescent. Nevertheless, in most cases it was impossible to obtain a sound casting. The last stages of solidification still led to small pipes forming in various parts of the upper surface down into the casting, and on rolling these broke up, causing the plates to be scrapped. In the end, better results were obtained by the method of vertical casting, using a sufficient weight of metal to allow for the removal of the unsound gate end.

It is difficult with some of these alloys cast in heavy weights to avoid all intercrystalline shrinkage. I think Bailey and Baker give two conditions for obtaining soundness and avoiding intercrystalline shrinkage. One is that unidirectional solidification should occur. That may be contrived. The other is rapid solidification. In the case of heavy weight castings, this constitutes a serious difficulty. It is impossible to extract heat sufficiently rapidly. Incidentally, with these heavy-weight aluminium bronzes the Durville method of casting, which is so useful with the lighter weights, is virtually impossible.

On the subject of nickel silver, I think the description by Bradbury and Turner of their process is as complete as any I have ever seen of a works process. It gave me the feeling that one could hand over the process to some one quite inexperienced and simply tell him to follow the instructions.

I should like to put a question to the authors with regard to a point on p. 386, where they state, "The caster first charges the nickel shot and then the heavy pieces of copper. The zinc is placed around the sides of the crucible and the scrap is fed in to fill up to the top of the trunk." I take that to mean that the zinc is charged at the same time as the other materials, and if so, does not that lead to a very high zinc loss? Our own practice would be to add the zinc at a later stage.

No doubt there are good reasons for the continued use of the pot-casting method for nickel silver, but I think Mr. Campbell touched on this point this morning, when he hinted at the question, Why use that process at all? We have changed over in very large part to the use of Ajax-Wyatt furnaces for the casting of nickel silver, and there is no doubt that the product is substantially better. The difficulties over carbon intake are, of course, eliminated. It is difficult to find a lining which will stand up for long to the melting of nickel silver, particularly of high nickel content; but even with the reduced life of furnaces, it is still—apart from the technical improvement of the product—a paying proposition to melt in Ajax-Wyatts. We find that it is necessary to charge the materials more or less continuously in order to prevent the temperature from unduly rising.

While on that subject, I should like to ask the authors of that paper what they consider are the reasons why manganese, in the first instance, and phosphor copper, in the second instance, bring about undoubted improvement in the product; and particularly—I think I have this correctly—why does the use of phosphor copper tend to eliminate the tendency towards fire-cracking?

At the risk of repetition, I should like to refer to a point made by Mr. Davies this morning on the subject of the use of bone-ash mould dressing. As far as I know, in the casting of tough-pitch copper there is no substitute for bone ash. During certain stages of the war this created a very serious embarrassment. I feel that it cannot be true that bone ash is the only dressing. If it were, one would have to conclude that had there never been bone ash, there would never have been tough-pitch copper.

Speaking generally, I should like to recall the statement of Cook and

Fletcher that knowledge is available on nearly all the points connected with non-ferrous casting, and that the great thing is to apply the knowledge that already exists. Nowhere is that point brought out better than in the paper by Waddington.

I conclude on this note. I regard the organizing of this Symposium as the making of a casting. I think the papers provide the primary dendrites. The speakers have been filling in the intercrystalline spaces. There has been a great absence of surface defects and what I might call gas porosity. I think we shall end up with a very sound casting.

MR. P. F. HANCOCK *: I should like to contribute a few comments on the subject of this Symposium from the viewpoint of electric melting.

Bailey and Baker, in the section of their paper devoted to preparation of the molten metal, stress the importance of avoiding gas pick-up and of elimination of gases if unavoidably present in the melt. Hydrogen, present in the molecular form, or generated by reaction of water vapour with constituents of the melt, is undoubtedly the most serious offender.

While reasonably satisfactory measures are available in many instances for elimination of hydrogen, surely the better approach to the problem is to avoid its presence altogether during the melting operation. Water vapour, and sometimes hydrogen, in contact with the melt are practically inseparable from the operation of fuel-fired furnaces. With electric melting, on the other hand, a clean dry atmosphere can be maintained at all times, either oxidizing, neutral, or slightly reducing in character, whichever best suits the particular metal or alloy. Under these conditions, the possibility of hydrogen pick-up is minimized, and, if it is already present in the melt from raw materials or other sources, the most favourable environment is created for its elimination.

This point is admirably brought out by Waddington in his paper, where he describes the practice at Copper Cliff for melting of cathode copper in large arc furnaces. As he indicates, the furnace atmosphere can be altered at will by drawing a controlled and variable amount of air through the melting chamber. The typical atmosphere composition which he quotes, about 17% CO₂, 3% CO, and traces only of hydrogen and water vapour, must approach the ideal for this particular operation, and could be bettered only by going to the vacuum technique; the advantages accruing therefrom, as compared with the previous reverberatory furnace practice, are fully emphasized in his paper.

In connection with the question of furnace atmospheres, I think we need to be rather careful about our terms. There is a tendency to talk rather loosely of oxidizing or reducing atmospheres without any indication of what materials they are oxidizing or reducing to. For instance, an atmosphere can be reducing to copper and oxidizing to some other constituent, or *vice versa*. I think it is true to say that an oxidizing atmosphere high in water vapour may, with many alloys, be more deleterious than a slightly reducing atmosphere, which is free from hydrogen and water vapour, and contains only CO as a reducing constituent.

In the melting of brass, unlike most non-ferrous alloys, gas pick-up is of minor importance, and it is surprising, therefore, to find that this is the field in non-ferrous practice where electric melting has achieved its widest use. As Cook and Fletcher indicate in their paper, the low-frequency induction furnace has become practically the standard melting unit for tonnage production of brass for ingots. It was interesting to hear from Mr. Bolton that it is also being used to an increasing extent for nickel silver. The low-frequency induction furnace is difficult to use where smaller outputs of varying analysis are required, and here it would seem that the rocking-arc furnace has much to

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recommend it. It has achieved a wide measure of success in America, though it has not been used to any marked extent in this country. This may be due to the widespread impression that zinc loss is excessive in this type of furnace. In point of fact, zinc loss may readily be held to very reasonable limits, ranging between 1 and 2½%, according to the alloy, the size of the furnace, and the form of the charge melted. The higher figure relates to a small furnace of the order of 50–100 lb. capacity, with turnings and other finely divided material forming a large proportion of the charge.

In view of the clear advantages of electric melting as instanced by its wide acceptance for brass melting, one may wonder why it has not been more often adopted for other non-ferrous alloys. In particular, the bronzes come to mind, where all the advantages present in brass-melting practice apply equally, and in addition there is the further virtue of avoidance of gas pick-up. In the bronze foundry, the latter point has begun to be appreciated, and a number of electric furnaces, particularly of the rocking-arc and rocking-resistor types, have been installed in recent years. For ingots, however, there have, to my knowledge, been very few installations of electric melting equipment in this country, although the advantages which have been amply proved in the foundry would appear to be of equal value in ingot production.

An earlier speaker referred to the very large amount of scrap which is produced in the non-ferrous, particularly the bronze ingot, field, and some reduction of this scrap production would presumably result in a considerable saving of production costs.

These remarks apply equally to a number of other classes of non-ferrous alloys—the aluminium alloys, for instance—and no doubt as time goes on the electric melting furnace in one form or another will be increasingly adopted in these fields.

MR. F. HUDSON * (Member): The six papers forming this Symposium are indeed most interesting and there are many points open to discussion. Personally, I would like to confine my remarks to two aspects, namely structure and the process of solidification.

Bailey and Baker in their paper, indicate quite rightly that the ideal structure to be aimed at in billets and ingots for subsequent working should preferably consist of uniform equi-axial grain, free from preferred orientations and large individual grains. It would be interesting to learn how many producers to-day value this point and endeavour to obtain it by actual production methods as distinct from having it done for them by the use of an alloy of particular composition. Quite apart from the improved workability shown by ingots and billets possessing a uniform equi-axial grain, such a structure also plays a most important part in the process of solidification by promoting maximum solidity and reduces the tendency towards segregation and shrinkage porosity. It is appreciated that degree of quality in many cases is determined by commercial considerations. For example, the producer of brass ingots may have to take less precautions in this direction than the manufacturer making material which has to be ultimately employed for highly stressed parts working under severe service conditions embodying heat or corrosion. Under these latter conditions the quality of ingots and billets from the metallurgical point of view must always be as high as possible. Furthermore, so very often non-ferrous alloys in this class are of a composition prone to give coarse columnar macrostructures and are generally produced from relatively small billets or ingots, cast in metal moulds, which does not simplify the problem. In addition, many of these alloys lack fluidity and have high liquid shrinkage.

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What then is the best commercial method for casting such alloys in order to obtain ingots of uniform equi-axial grain? Quite a few people in this country to-day would be interested in the answer to this problem, and personally I would be glad if any of the authors contributing papers to this Symposium could see their way to express their views in this direction. As a matter of interest it might be noted that the nearest approach to what I have in mind is the casting method developed by Willcox, covered by U.S.A. Patent 1,926,573, and taken out in America in September 1933. This method, as shown in Fig. H, Plate CXXIX, taken from the patent specification, combines a high-frequency melting furnace and a high-frequency-heated ingot mould. Pouring is effected on similar lines to the Durville process as outlined in the paper contributed to this Symposium by Murphy and Callis, except that solidification of the metal within the mould is also controlled by high-frequency heating. So far as one can determine this process of casting has not been used or patented in Great Britain, and for the production of high-quality ingots in non-ferrous alloys of specialized type it would appear to have many advantages over the more orthodox methods in use to-day.

DR. O. H. C. MESSNER * (Member): I should like, first, to congratulate the Institute on choosing such an interesting subject for this Symposium. The various papers have been of great interest to the Swiss brass industry. Now that the brass industry in Switzerland is in a minority as compared with the light-alloys industry, we who belong to the brass industry have been very glad to get some information on what our friends on this side of the Channel are doing. It might be that the people in the light-alloy industry are a little bit more advanced in this field, and consequently might be in a better position to talk on the subject at this meeting.

In the light-alloy field the semi-continuous casting process has been developed to a great extent. They have a much closer control than we have in the brass industry, where the trial-and-error method is still to some extent used.

Most of our furnaces—indeed, I think I might say all of them—are electrically heated. Because of restrictions on the use of coal and other fuels, we had to shift to high- and low-frequency furnaces and, to a lesser extent, to rocking-arc furnaces. Consequently, all development has been on these furnaces, and we have not been able to consider using any oil-fired furnaces. Only the electrical heating of crucibles used as ladles for pouring is sometimes a difficult matter, and we are facing some troubles in that direction.

I have noticed in the paper by Bradbury and Turner that for nickel silver, crucible furnaces are still used to a great extent. For a good many years we have used the high-frequency as well as the low-frequency furnace for nickel silver, and after long discussions on the relative advantages and disadvantages we finally found that the low-frequency furnace, namely the Ajax-Wyatt, as actually used in a brass foundry, is in every way the most suitable for the production of at least several tons.

The main disadvantage of this furnace when used for nickel silvers is the comparatively short life of the linings. With even the better qualities of ordinary linings, there is a life of only about 100 melts with an 18% nickel silver. We have been able to do much better with linings which were originally developed for melting zinc and zinc alloys in the Ajax-Wyatt furnace. These linings, which are similar to some used in the U.S.A. (known as cupola patch), have given a life of between 200 and 400 melts for nickel silver containing about 18% nickel. I wonder whether in Great Britain other linings which give a longer life are used.

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We do not consider the Ajax-Wyatt furnace is suitable unless it gives a life that is longer than 100 melts per furnace before relining. If the life is shorter, as is the case with certain alloys of high nickel content, we still prefer the high-frequency furnace, in spite of the higher current consumption.

You may be astonished to hear that we in Switzerland sometimes face very great shortages of electricity. St. Peter very often does not give us enough rain, and as we depend entirely on hydro-electric power, the situation becomes very difficult, particularly in the winter season.

For this reason we are thinking of again putting in emergency melting units with oil and coke firing. Personally, I do not think the solution should be sought in this direction, but rather that we should have ample capacity and put castings into stock to cover the short period during which we are unable to melt because of the shortage of electric current. The advantages of electricity are so great when compared with the former system of melting with oil and coke furnaces that we would not think of going back to that system.

In the casting field we in Switzerland are still not quite certain about our procedures, and I think it is in this direction that we have most to learn. The human element is becoming a more and more important factor. In all countries we find that the workman no longer has the same devotion to his work, and we have to try to remedy this state of affairs as far as we can. I should very much like to hear how far our English and American friends have gone with, for instance, temperature control. In Switzerland we are not able to go in for continuous casting in the brass industry because we have about 150 different alloys to cast, and though normally about 100 of them could be cut out without any trouble, it cannot be done now because of the market situation. Continuous casting can therefore be used only on a certain reduced part of the total production. On the other hand, temperature control might be possible on all furnaces. I noticed in an American brass foundry that they controlled all castings without exception in brass and nickel silver before pouring, and they gave their caster the green light when he was right with the temperature. I feel that in that way we can certainly cut out to some extent the human element.

We use both the so-called flaming and non-flaming dressings in foundries, but for the water-cooled mould the flaming dressing is used exclusively. We feel that there is still room for further improvement with the mould dressings, and I should like to ask whether other sorts of mould dressings are used in Great Britain. I noticed in the U.S.A. that they added soda ash to mould dressings. I recently heard that a Continental metal works is using resin, or "Kolophonium", as we call it in German, with oil as a mould dressing for water-cooled moulds. I know that this has been used for a long while on cast iron moulds and is applied hot, but in this case it is applied as a paste on water-cooled moulds. In order to increase surface quality, we have also recently tried some aluminium oxide paints similar to the mould dressings mentioned in papers by Dr. Pell-Walpole in the *Journal* of the Institute. We have not yet come to any conclusion as to the advantages and disadvantages, although the first results have been rather promising.

We are also trying to improve the surface quality by various working procedures. Some thirty years ago castings were worked at the surface by scraping according to very crude methods. There was an improvement later on with the Junker type of pendulum milling machine and by other surface milling methods. The American brass industry has gone in a different direction and is milling exclusively after hot and cold rolling at a thickness of the slab of about $\frac{1}{2}$ in. I should like to hear how people in Great Britain are dealing with castings after casting—whether they are shaving the surface by some means, whether they are milling, whether it is done before or after hot

rolling, or whether it is not done at all. The question of the nature of the surface defects may be of some importance in this respect.

With regard to surface cracks, particularly with nickel silvers cast in a water-cooled mould, we have found a process which has helped to some extent: we break down the slabs 10 or 20% in some first passes before milling the surface. The cracks have then developed and are machined off, and subsequent working does not cause any defects. Nevertheless, this is a costly procedure, and we have found by comparative tests that the trouble can be overcome by suitable mould dressings only.

I wonder whether in England the semi-continuous casting process, so-called "Wasserguss", has been considered for brass or other non-ferrous foundries apart from aluminium foundries, where it has been used for quite a while. The process seems to offer a great number of advantages. It is slower than the Junker-type moulds, but in view of the difficulties arising as a result of the fact that the brass industry is to-day using much more scrap than before the war, I wonder whether this method might not be of advantage in many respects, even though it is not so efficient as fully continuous casting.

I was very pleased to hear this morning that the use of the Soro process is being considered in England. This method was developed quite a time ago, but it has been used only for bars. In Switzerland we do not think that for brass bars the Soro process will offer a great advantage when compared with the ordinary extrusion methods; but it certainly has many advantages in the case of alloys which cannot be extruded. We are considering using it for the casting of slabs, which may be a new application, and in which it seems to have advantages in many respects. It gives a very clean casting and the machining of the cast ring is much easier than that of a straight slab, which requires much more complicated machines. In the case of nickel silvers and some brasses, it may be of great use in the future. We have great difficulties in producing leaded alpha-brasses, and we hope that the Soro process may offer us a solution, although the tests have not yet been completed.

May I say, in conclusion, how much I have enjoyed being present at these discussions.

MR. E. A. G. LIDDIARD,* M.A. (Member): This Symposium enables us to assess the progress that has been made in our understanding of the mechanism of casting and solidification of metals. This understanding has been largely due to the work of the British Non-Ferrous Metals Research Association, and in particular to the early work of Bailey and his collaborator, Dr. Genders, on the casting of brass ingots, and to the more recent work of Baker and his colleagues. I regard this Symposium as something of a personal triumph for those workers.

I shall confine my remarks to the paper by Bailey and Baker, a paper which seems to me to crystallize, without any significant defects, our knowledge of a complex subject.

One has to search very carefully for points in the paper on which to comment other than to express wholehearted agreement. I should, however, like to deal first with a few minor points.

The first is on p. 287, where the authors, in referring to surface exudations, say that "such exudations can only occur after the bulk of the ingot is sufficiently rigid to allow contraction away from the mould face. . . ." It does not seem to me that the bulk of the ingot has to be at all rigid. As soon as a comparatively thin skin of metal in contact with the mould face has formed, there will be a tendency for it to draw away from the mould wall in those areas where there is a very low hydrostatic head, e.g. just at the point

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of entry of the flow of metal from a Durville-cast ingot. Lower-melting-point constituents at the grain boundaries of this skin tend to remelt owing to the flow of hot liquid beneath this skin, and there is a greater risk of exudations at this point than in other points of the ingot where the hydrostatic head is sufficient to push back or to hold the skin in contact with the cooler mould face.

On p. 289, at the top, it is implied that impurities forming ductile grain-boundary films will not cause hot-shortness below the solidification temperature of these films. I doubt if ductility is as important as tensile strength relative to the material of the grains. In some work we have been doing at the Fulmer Research Institute on aluminium-tin alloys, consisting essentially of aluminium surrounded by tin, weakness develops well below the melting point of tin and at slightly raised temperatures which we ascribed to the low tensile strength of the tin at slightly elevated temperatures where the tin has very low strength relative to the aluminium. The films are so thin that their high ductility does not become significant, and the extension of the thin tin films, although probably high in relation to the thickness, does not sufficiently work-harden the tin to allow it to carry sufficient stress to deform the aluminium crystals. In these circumstances the ultimate tensile strength of the impurity films in relation to the grains is of more importance than their ductility. One can imagine, on the other hand, that a high-strength impurity film, even if without ductility, might cause no significant grain-boundary weakening, provided that the stress necessary to cause deformation of the grains is below the ultimate tensile strength of the brittle grain-boundary constituent.

On p. 296, in referring to chlorine degassing, the authors imply that chlorine is insoluble in aluminium. I do not know of any direct evidence on this point, but I know that in practice in one foundry the metal is always allowed to stand for a short time after chlorine degassing, since the foundry staff claim that, in their experience, casting immediately after chlorine degassing gives gas unsoundness. They infer that chlorine has some solubility, but that the chlorine diffuses away rapidly on standing in air.

Bailey and Baker go on to say that the free energies of chlorides of aluminium and hydrogen at the temperatures involved makes it practically certain that combination between hydrogen and chloride is negligible and that degassing is effected by a scavenging action. I hope that they have kept in mind that the hydrogen is probably dissociated on the surface. Some experimental work which Dr. Gross and his colleagues are doing at Fulmer on the reaction between aluminium trichloride vapour and aluminium in the presence of oxide films and with and without traces of water vapour may incidentally throw further light on this.

On p. 306 the authors refer to the fine structure produced by rapid cooling in the "tin-can" method of casting. In some circumstances the rapid directional solidification can cause columnar crystals to form along the axis of the ingot, and the chief merit of this casting method is, in my opinion, the high degree of soundness and freedom from gas porosity that results from the directional and tranquil solidification of the metal.

This brings me to a point that I have raised previously in discussions here. I believe that tranquil solidification has a virtue, apart from the avoidance of trapping of oxide films or mould gases, in preventing or delaying the initiation of bubbles of dissolved gas. I will not go fully into this again, but would refer those interested to the discussion on papers by Fox and Baker which were published in the 1945 *Journal*.

The main points of my contention were that under tranquil conditions very considerable pressures were necessary to initiate a gas bubble in a liquid since the difference in pressure between the inside and outside of a bubble $P = \frac{2s}{r}$.

where s = surface tension and r the radius of the spherical bubble. When r is very small P must be very large. When the liquid is agitated, however, vortices are set up and the pressure difference required for the initiation of the bubble becomes very much smaller. Experiments by Dean and more recently by Temperley have demonstrated that if a sealed glass vessel containing water and a very small air bubble is heated until the bubble disappears and then cooled again, taking every precaution to avoid agitation, the bubble of air does not reappear until a very considerable negative pressure (from — 50 to — 150 atmospheres) has been developed inside the container. The negative pressure was calculated from the distortion of the glass container with known elastic characteristics. A slight tap on the sides of the container caused the immediate release of the gas as bubbles. A simple, and to me, at any rate, delightful experiment, which demonstrates this point is to open a bottle of beer very carefully and without shaking it. If the contents of the bottle are then poured out in a turbulent manner, you will see at once how the turbulence assists in the release of gas bubbles.

Degassing of metal by supersonic vibrations is another illustration of this principle, and when the authors say on p. 295, in comparing the mode of entry of hydrogen into aluminium from water vapour and dry hydrogen, that the result implies that when the internal gas pressure exceeds one atmosphere bubbles are formed and escape, this I think will take place only under the conditions which they describe in which the melt is agitated.

I think the thing to be aimed at is to agitate the metal before it starts to solidify so that you can get all gases out of it, but if you fail, then solidify under the most tranquil conditions.

I think it is evident that the careful study of solidification mechanism which is epitomized in the paper by Bailey and Baker has produced and is still producing many important advances in detail which have resulted in improved quality in ingots, but we are still a long way from producing perfect ingots; and I think there is a challenge here, which should be accepted, to depart as soon as may be from the old traditional methods and apply our knowledge and ingenuity to the development of more-scientific casting methods.

MR. R. W. RUDDLE,* M.A. (Member): The term "directional solidification" is mentioned in a number of the papers in this Symposium and has also been mentioned quite frequently in the discussion, and since this term seems to be used somewhat loosely on occasion, especially when it is prefixed by "uni-", a few words on this subject may not be out of place.

I therefore propose to define "unidirectional solidification", to discuss how far this is attained in practice and ways in which the directionality of solidification can be improved. For simplicity I shall confine most of my remarks to the case of top-poured ingots, and I shall assume that the metal or alloy being cast has no freezing range, so that the solid and liquid regions in the solidifying ingot are sharply divided.

Let us first of all assume the mould to be filled instantaneously with molten metal. For true unidirectional solidification to occur, solidification must obviously take place from the base of the mould upwards, the solidification front being a plane parallel to the base and there being no solidification at all from the side walls of the mould (Fig. J).

Under conditions of rapid pouring this state of affairs is never attained or even approached in practice. Under these conditions the shape of the solidification front will be roughly as in Fig. K, and it is evident that, even if the ingot is well supplied with feeding metal, there is considerable

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danger that centre-line shrinkage or secondary pipe formation may result. Slower rates of pouring, by allowing time for solidification at the base of the ingot to become well advanced before freezing commences at the top, modify the shape of the solidification front in the way shown in Fig. L.

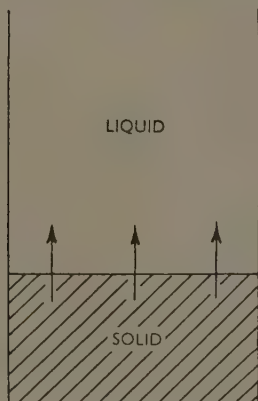


FIG. J.

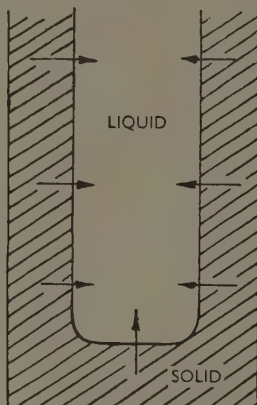


FIG. K.

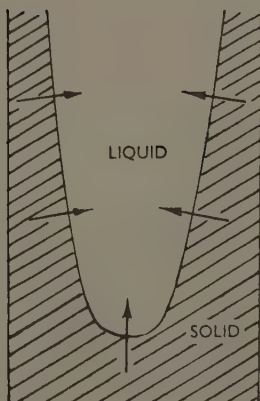


FIG. L.

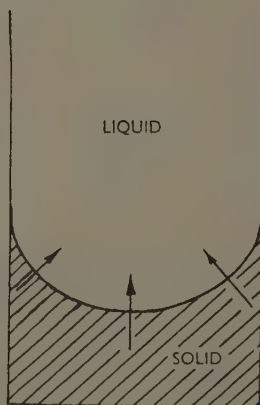


FIG. M.

It is clear that with a solidification front of this shape, there is much less danger of bridging of dendrites in the upper part of the mould and of centre-line shrinkage occurring. It is also clear that the shallower the cup formed by the solidification front, the sounder will be the ingot. A further advantage of the

shallow cup is that there is less likelihood of setting up dangerously high internal stresses in the ingot. The production of a shallow cup-shaped solidification front should therefore be the aim of those responsible for ingot mould design and casting procedure. There are two ways of obtaining the desired state of affairs. First, the mould should be designed in such a way that most of the heat in the ingot is removed through the base and the least possible amount through the side walls. Secondly, the slowest practicable rate of pouring should be employed, since the depth of the cup formed by the solidification front is greatly affected by this factor.

It is interesting to note that this is exactly what has been done in the casting of aluminium alloy ingots by the direct-cooled continuous casting process. Here the use of very low pouring rates coupled with a high rate of heat extraction in a vertical direction produce a shallow cup as illustrated in Fig. M.

Incidentally, the advantages of slow pouring are exemplified in the paper by Bond-Williams, who obtained a great improvement in the soundness of phosphor-bronze ingots by increasing the pouring time by a factor of six. Murphy and Callis in their paper discuss the bottom-run mould patented by Durville. From the point of view of directional solidification the design of this mould is extremely bad, especially since the ingot is of necessity poured slowly. A better procedure would be to arrange for the ingot to be fed from the bottom with freezing at the top accelerated by water-cooling or other means.

I should like to turn now to some other points raised in the papers. Bailey and Baker suggest that the degasification of aluminium alloys is more readily effected with chlorine than with nitrogen, but I wonder whether this is really true. In my experience the two are about equally effective with most aluminium alloys, but with alloys containing substantial quantities of magnesium, nitrogen is the more effective degasser. A reason for this is not far to seek. In magnesium-free alloys the chlorine released from the degassing tube at the bottom of the pot reacts with the aluminium to form bubbles of aluminium chloride gas which pass up through the melt, thereby removing the dissolved hydrogen much in the same way as nitrogen bubbles do. When magnesium is present, however, magnesium chloride is formed preferentially—this can be shown thermodynamically—and since this substance is a liquid at the temperature involved, the size of the bubbles diminishes rapidly as they float to the surface. This obviously reduces the efficacy of degassing considerably.

There is one further small point I wish to make. At the beginning of their paper, Murphy and Callis state that no figures are available for the heats of fusion of aluminium bronzes. This is so, but I should like to point out that reasonable estimates—to within about $\pm 10\%$ —may be obtained by the use of the mixture law, at least for the binary alloys. The heat of fusion for a 90 : 10 alloy is thus calculated to be approximately 55 cal./g.

MR. W. E. BALLARD * (Hon. Member of Council) : It is some years since I was actively engaged in the production of castings, and in the short time at my disposal I would like to confine my remarks almost entirely to the question of flaming dressings. The authors of the papers in the Symposium have all given some thought to these mixtures, and Mr. Waddington has described in detail the manufacture and maintenance of the compound which will give the best service under the standardized and controlled methods that he used, but I think that Bailey and Baker dismiss the question too lightly when they say there is no reason to suspect that one oily vehicle is better than another.

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If one examines the published tables showing the physical and chemical properties of oily substances such as petroleum jelly, rape oil, seal oil, &c., there appears to be no clue to work upon, yet I think it would be agreed, that if a caster who is used to getting good surfaces with rape-oil mixtures is suddenly given a mixture of petroleum oil, the surfaces of his billets will deteriorate, and if this is so, I submit there must be good reasons.

It is pointed out that one function of the oily material is to produce in the mould a smoky reducing atmosphere. Some years ago I took samples of the gases in moulds in which brass was being poured, the mould dressing being in one case mixed with vaseline, in the other with rape oil. The heat of the metal apparently had a cracking action on the carbon compounds and the gases consisted of simple hydrocarbons in either case, in which were suspended particles of carbon forming the smoke. It would appear that it is unlikely that the chemical action of two dressings in respect of the metal will be different.

It appears to me that the main function of the oil is to hold upon the surface of the mould a layer of material which will prevent the sticking of the molten metal. The layer of dressing must be even and adherent. Graphite, charcoal, and bone ash all seem to give such inert uniform layers, provided that they are sufficiently finely ground and that they are dry. In the past too little attention has been given to the dryness of the powder. Finely ground dry powders are difficult to wet, and it seems that the surface of some powders are more difficult in this respect than others. The properties of viscosity and surface tension of the oily vehicle, at the mould temperature, may therefore be very important.

I have last week carried out a few experiments by mixing 10% by weight of fine bone ash and charcoal in petroleum jelly, rape oil, and seal oil, and then having made the mix, investigating how the mixture could be spread on a glass slide at various temperatures. By simple tests such as this, it is easy to find that vaseline mixtures do not spread easily below 100° C. and that seal oil is much inferior to rape oil, in producing a satisfactory film. Such tests as these could be expanded and I think could produce quite a fruitful field of research which would once and for all dispose of the question of production of flaming mould dressings.

A previous speaker in the discussion has mentioned the possibility of the addition of other chemicals to the dressing, and I remember years ago it was a habit in some cases to introduce dry powdered salt into the mixture. It is certain that this salt did tend to give brass castings a very bright finish, but it scoured out the cracks of the moulds that have been referred to in other papers, and hence mould deterioration was extremely rapid. It appeared that on the metal interface chlorine or hydrochloric acid gas may be generated which gives this scouring action. In any event the addition of salt did not seem to be a good idea.

Finally, I think the Institute and the authors are to be congratulated on these papers which have permitted this discussion, and this Symposium surely points the way to providing the practical man with the papers which he has been demanding.

DR. J. W. CUTHBERTSON * (Member) and DR. W. T. PELL-WALPOLE † (Member): My former colleague, Dr. Pell-Walpole, had hoped to be here this afternoon, but his household is in the throes of influenza, and he therefore sent me a few notes and asked me to deputize for him; so my comments should be regarded as a joint contribution.

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† I.C.I. Research Fellow, Metallurgy Department, University of Birmingham.

The papers presented in this Symposium comprise a unique collection of authoritative information on the subject of ingot casting, from both the theoretical and the practical aspects. The Committee, the individual authors, and the industrial organizations concerned deserve the warmest thanks of the Institute as a whole.

We propose to confine our remarks entirely to the melting and casting of bronze.

With regard to the specific scientific advances represented by practices which are described in these papers, we wish to comment on the one by Mr. Bond-Williams, dealing with the casting of phosphor-bronze ingots. Mr. Bond-Williams was the first bronze manufacturer who was bold enough to apply to industrial practice the results of our laboratory scale researches on flux degassing and slow pouring. His paper is therefore a special pleasure to those who are concerned in these researches, for the most satisfactory reward to anyone who has carried out researches of this type is to see the results of those researches applied successfully to industrial practice, with improvement in the quality of the product and without injury to the economics of the process. In general, manufacturers and scientists alike are bitterly aware of the gulf which so often exists between laboratory research and its application to industrial practice, and Mr. Bond-Williams has earned the admiration of both for his marked success with so formidable a task.

One factor which seriously affects ingot quality and which we feel has not been sufficiently stressed is mould dressings, viewed more particularly as a source of hydrogen contamination. Our experience in the casting of bronze in chilled moulds is that certain brands of aluminium paint properly applied give good results—the best results, in fact, of anything of which we are aware.

A point which comes to mind in reading Mr. Bond-Williams's paper, although it has no direct bearing on it, is the question of phosphorus content in bronze. The bronze manufacturer is frequently called upon to produce material containing say 0.25% of phosphorus or more, merely because his customer demands high phosphorus without any specific reason for it. This seems to be largely a matter of tradition. It is a very unfortunate tradition because the difficulties which beset the bronze maker in hot-working bronzes diminish as phosphorus content is reduced. There is no difficulty in industrial practice in producing bronze with substantially less than 0.1% of phosphorus, and it is even possible to go down as low as 0.02%, which is regarded generally as the safe minimum to ensure freedom from tin oxide. Perhaps in the future the users of bronze will realize that a high phosphorus content is not always necessary, and when they do the hot working of bronze will become somewhat easier. We are speaking particularly of bronzes containing more than 4% tin.

Bailey and Baker have referred briefly to developments in the continuous casting field, and we would like to amplify their remarks. Undoubtedly one of the most interesting and far-reaching developments in the recent technology of bronze casting is the introduction of the continuous casting process. Other metals and alloys have previously been, and are being, continuously cast with success, but the application of this method of casting to bronzes of all types is a new departure. A considerable weight of bronze is used in the manufacture of wire and bushes, and for these purposes bars of relatively small diameter in as long a length as can conveniently be handled are wanted. The production of such bars by conventional methods of casting presents considerable practical difficulties. The flux-degassing process devised by Dr. Pell-Walpole, coupled with the slow pouring which he recommends, certainly ensures that the metal itself will be sound, but to produce a perfectly sound casting from it in the form of a bar, say, 8 ft. in length and an inch or two in diameter by casting in the customary chill mould is almost an impossibility. In making

such a casting the metal cannot be prevented from splashing against the sides of the mould, and even under the most favourable conditions the upper and lower ends of the bar will have to be discarded. The alternative of casting a larger-diameter ingot and reducing it to the required dimensions by hot or cold rolling is expensive, time-consuming, and with some compositions almost impossible.

Continuous or semi-continuous casting affords a means of overcoming these troubles and simultaneously of effecting considerable saving in production costs. Long lengths can be produced and dimensional tolerances can be held much more closely than by any other casting method. Further, cored bar can be made almost as easily as solid bar, and if other than a circular cross-section is wanted this again presents no special difficulties. One firm in America has been producing continuously cast bronze for well over a year and is finding a ready market for its products. These products include binary tin bronze containing up to 10% tin, leaded bronze, gun-metal, and leaded gun-metal. Rods and tubes having a maximum diameter of $4\frac{1}{4}$ in., and also rectangular sections, in lengths of 10 and 16 ft., are being made. This type of material is proving particularly acceptable to the American automobile industry, as the long straight lengths available are extremely suitable for handling in high-speed automatic lathes and screwing machines, and it is also said to be finding an outlet in the manufacture of Fourdrinier wire.

With the manufacturing methods employed in this country it is doubtful whether there would be a sufficiently large demand for continuously cast bronze to warrant the installation of the large and expensive type of continuous casting plant which has been developed in America. These large plants become uneconomical as soon as they are operated a little below their maximum rated output. In this country the demand is likely to be smaller and the diversity of composition and dimensions possibly greater than in America, and it is believed that this demand will best be met by a semi-continuous process, by which bars of up to about 10 ft. in length can be produced in a variety of bronze compositions as and when required. To do this does not involve any great expenditure on complicated plant, and several bronze makers here have, in fact, succeeded in producing continuously cast bronze bars of a high quality using simple equipment.

The essential points to be considered in the construction of a machine for the continuous casting of bronze have been enumerated in a recent article by Pell-Walpole and Kondic.* They are:

1. The method and rate of feeding the molten bronze into the die;
2. The material of the die and method of cooling;
3. The mechanism for extracting the solidified metal continuously from the die.

It is not proposed to enlarge upon these points at this juncture, as they are dealt with fully in the article just mentioned. It will be sufficient to say that preliminary difficulties in designing and building a semi-continuous casting machine for handling bronze have been largely overcome, and that most promising results have been obtained both in the laboratory and in those works which have experimented with the process.

The properties of continuously cast bronze are excellent. Structurally, bars made by this process show an axial zone of columnar crystals surrounded by very fine equi-axed crystals, the relative amounts of the two types of crystal varying with the dimensions of the casting and with the casting conditions. Continuously cast bronze is extremely free from porosity and when properly made has an excellent surface, free from tin sweat.

* *Metal Ind.*, 1949, 74, (11), 203.

It is realized that this Symposium is primarily concerned with the melting and casting of ingots for working, and in raising the subject of continuous casting we would, therefore, point out that while our remarks have been concerned to some extent with a method of producing material which at present is being used mainly in the cast state, there is also a big field for the application of continuously cast bronze in wrought form. This applies particularly to its possibilities in the manufacture of wire. Much bronze wire, especially in the higher tin ranges, is made by the laborious process of cold rolling and annealing preparatory to the actual wire drawing, starting with a long ingot of small cross-section. There is no reason why an ingot of substantially smaller cross-section, necessitating less work in reducing to the final dimensions, should not be continuously cast and, owing to the superior properties of the continuously cast alloy as compared with those of castings produced by pouring into a chill mould, the reduction process should be facilitated.

DR. A. G. RAMSAY,* B.Sc. (Member): I have been out of touch with metal casting for some time, and therefore I feel a little diffident in joining in this discussion, but the matter is of such wide interest that I cannot resist doing so.

The first point I should like to mention is the term "dissolved gas" which is used in several of the papers and which, I am afraid, is used fairly loosely by metallurgists generally. In the papers, where the authors have referred to dissolved gases they mean gases which really dissolve and which do not form compounds, and in some cases they have actually specified that gas as hydrogen.

I suggest that it would be of great assistance to the practical caster if we made up our minds and told him that the only gas that really does dissolve in metal is hydrogen, because that seems to be substantially true. Any other gases which do dissolve, dissolve to such a slight extent that the matter is still controversial. If one meets gaseous-porosity troubles not due to hydrogen, they are due to compounds, such as oxides, sulphides, &c., which have formed in the metal and which interact.

In this connection, in the mention of Bailey's theory to account for the low solubility of gases in brasses, it is implied in one of the papers that air and sulphur dioxide are quite inert to brasses. That would be a dangerous thing to tell any caster. The gases do not dissolve, but are by no means inert. We are just fortunate that the products of their reaction with brass are easily removed from the molten metal.

In the first paper there is mention of the effects of gaseous porosity and how, particularly if it is due to hydrogen, the defect of porosity may be overcome by the gas diffusing out when the metal is worked and the cavity healing up. I have often wondered in that connection what happens in tough-pitch copper, where there is porosity and the gas is steam which cannot diffuse away—and yet the minute holes will heal up in working. I think it must be that under the pressure applied during working the steam reacts to form cuprous oxide and hydrogen, and the hydrogen can then diffuse away. Why is it that when the pores become larger, that does not happen, and the casting is defective? I think it must be a matter of time. When there is a larger amount of gas and the casting passes through the rolls, the time of application of pressure is not long enough to carry the reaction sufficiently far to enable the gas to diffuse away.

Turning to some of the remarks on the casting and melting of brass, I have been very interested to learn that in some cases, apparently, in low-frequency melting to-day almost as much metal is left in the well of the furnace

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as is poured out for casting. Presumably that is done so as to obtain rapid immersion of the cold charge to reduce losses. If the well is kept as deep as that, I am wondering whether the losses could not be reduced even further by omitting skimming from some of the charges.

Twenty-five years ago I was investigating zinc losses (which, by the way, were enormous) from reverberatory-furnace melting of brass, and I found that nearly all the losses occurred when the dross was skimmed off the furnace, and that if one left that skimming to every third charge, the losses came down to a very low figure. That might be applied to the existing low losses of electric furnaces, and with the price of zinc as it is, may be worth-while.

Another point mentioned about low-frequency melting was that the thermal effects from the furnace are sufficient to ensure adequate mixing. My own experience has been that if the zinc is added at the very end of the melting, as is the practice in some melting shops, the thermal effects are not sufficient to mix that zinc in unless an inordinately long time is allowed after the metal is really molten.

A further point mentioned in the paper on brass is that segregation does not occur with 60 : 40 brass containing lead. My experience was that in making thin flat castings of 60 : 40 brass containing about 1% lead there was a segregation on the mould face, and it produced in the finished product exactly the wood-grain effect described by Bond-Williams in bronzes. It was very difficult to avoid that segregation.

I should like to associate myself with the congratulations that have been offered to the authors of the papers. The implications of the papers are that we ought to produce, and can produce, reliable and sound castings. If we do not do that, it is our own fault. This fact is a striking tribute to the progress which has been made. Cook and Fletcher go so far as to say, "Failure, therefore, to produce castings of satisfactory quality must be ascribable to an ignorance of, or a lack in the application of, the knowledge derived from long practical experience and specific investigations". One of those authors is a castings producer, and I think, therefore, this is a challenge to everyone.

It is interesting to note the different methods used by the various producers to meet that challenge. Some, such as Copper Cliff Refinery, use instruments very widely and lavishly and rely scarcely at all on the judgment of the men. Some of the others almost go to the other extreme, particularly where small units are used for crucible melting, and rely upon the judgment and skill of the operatives. I personally feel that the men are more likely to err, and I suggest that the future casting shop will have to be designed so that instrumental control can be effectively used.

PROFESSOR H. O'NEILL (*Rapporteur*): For a few remarks in conclusion it is noted that this afternoon we have heard still more about tranquil casting. I should like to remind you that in teaching metallurgy one has to extol both this method and centrifugal casting—the one in which there is quiet and the other in which there is much agitation. All the time that I was listening to the remarks about the desirability of emptying a bottle of beer very carefully, I was worried about having also to teach that one might shake it up quite a lot in order to get the best results. The point made by Mr. Liddiard about the prevention of the release of gas bubbles by tranquil casting seemed very interesting and important.

I am glad that Mr. Ruddie dealt with the term "unidirectional freezing" because to me it might mean the production of an ingot which had columnar crystals right from top to bottom. Metal freezing in one direction could be a series of closely-packed stalagmites, so to speak. What I think is meant in general is equi-axed crystal growth, but confusion arises if one is not careful about terminology.

From the Symposium I have formed the impression that electric melting is now very well established. One did not hear anybody deprecate electric melting for any reason whatever. Even when it was suggested that the capital cost was high, Mr. Campbell remarked that money was saved on other things such as chimneys.

I was surprised that nobody talked very much about nuclei in connection with macrostructure, but we heard something about mould dressings this afternoon, and Mr. Ballard's preliminary experiments are very interesting. It would be worth-while for somebody to continue with that kind of work.

Mr. Bond-Williams's explanation of the outlook that lay behind the form of his paper is understandable, but I do not think we must set too easy a standard. It is all very well to refrain from putting forward statements for fear of frightening people off, but decent men will respond to a high standard.

In conclusion, the Symposium seems to me to have been very well appreciated by the members who have attended. The presence of speakers from France and Switzerland has been a great pleasure to us. The printing of all the papers in one *Journal* of the Institute has been a great convenience and is a course that should be followed in any future meetings of this kind.

While the Symposium has been referred to as a landmark by many speakers, I do not think that there is any room for complacency regarding metal casting. There is still a lot to be done, but the spirit in which research and industry are beginning to go hand in hand augurs very well for the future.

MR. A. L. MOLINEUX : May I say a word or two in order to correct a misapprehension ? I have written a note to Mr. Brazener as follows :

Did I really say that I considered the Wigley furnace was not superior to the old type of furnace ? I certainly did not intend to convey that. What I wished to point out was that I was surprised that Mr. Bond-Williams still used the old type of furnace up to ten years ago. We use a modified Wigley type and have done so for twenty years, but we do not find that drawing air in from the outside makes any appreciable difference. I quite agree that the Wigley type does undoubtedly shorten the melting time.

I think that Mr. Brazener certainly understood something which I did not intend to convey in my remarks.

CORRESPONDENCE.

DR. F. A. FOX * (Member) : Messrs. Bailey and Baker are, in my opinion, to be congratulated on the production of a concise yet very readable account.

I would like to make a few observations on the casting of magnesium alloys for subsequent working operations. It was recognized long ago that a principal problem in cast pieces of this kind was the possible introduction into the billet of flux inclusions and of oxide and nitride skins. Both sides of this problem were solved well before the war : the flux-inclusion question was really a matter of the evolution of appropriate fluxes and fluxing technique. The body of the metal having been cleaned of small flux particles, the flux cover remaining on the surface of the metal (needed to prevent oxidation) had to be of such consistency and physical characteristics that it did not show any tendency to break away and to flow into the mould with the metal being poured.

The problem of oxide and nitride skin formation was not quite so easily

* H. J. Enthoven and Sons Ltd., London.

solved as for sand castings, where oxidation inhibitors could be mixed with the mould material. The solution aimed at was to reduce turbulence to a minimum, and also to attempt to achieve improved internal soundness by obtaining some directionality in solidification. The solution achieved was to provide the round billets (which were the only ones made at that time) with a slot runner and gate. The mould was steadily and smoothly filled by pouring down the bottom edge of the runner by means of an arrangement which permitted both mould and crucible to be tilted, the former sinking from about an 80° tilt back to vertical, and the latter tilting more, as the pouring went on. This procedure in some ways resembled the Durville process. The diameter of the runner might be about $1\frac{1}{2}$ in., and the slot-gate itself about $\frac{1}{4}$ in. or less across. A typical cast billet had the form of section shown in Fig. N.

The gate and runner were readily hand-sawn off. This combination of mould-form and procedure was very effective in reducing turbulence, and hence oxide and nitride skin formation. Other more minor precautions were taken, such as dusting with sulphur during pouring, and ensuring that the free fall from the crucible lip was small.

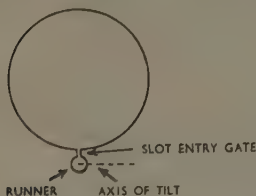


FIG. N.—Typical Cross-Section of As-Cast Magnesium Alloy Billet Made by the Older Process without Water Cooling.

At a later date, the production of stronger forging alloys in billet form became necessary, and hence the grain-size of the cast material, as well as the internal soundness, were critical. If the grain-size was too large, homogenization prior to hot working became a prohibitively long process, since the β phase at the grain boundaries had so far to diffuse. Some method of casting involving more drastic cooling and directional solidification was therefore needed.

The method then employed was what the authors call the "tin-can" process, except that an electrically heated hood was also used to bring the metal in the thin-walled mould to a uniform temperature before lowering it into water. This method was generally successful so far as the solidification was concerned, but had practical objections, in that, in the absence of a mechanical stripping device, the removal of the billet from the mould was troublesome. It was occasionally observed that, even under nominally standard conditions, some alloys, far from crystallizing with a fine grain, grew enormous grains of the order of a foot long. These were always alloys of the magnesium-aluminium type, and it is possible that this effect resulted from some circumstance which, for that particular mould-full of metal, had denuded it of foreign nuclei, which otherwise operated to produce the fine grain usually obtained with the process.

During the war the application of semi-continuous casting methods such as are mentioned by the authors, was made to magnesium alloys, with marked success. The attempt was, in the first place, made very gingerly, since molten magnesium and cold water is not a pleasant combination. It was found, however, that if large quantities of water were always employed, no unpleasant accidents were likely. In this process the small volumetric heat capacity of magnesium alloys played a special part, in that the control of the rate of lowering through the water sprays had to be particularly close to achieve uniform results. The necessity for this close control, coupled with the necessity for a smooth descent (otherwise strains might be imposed on the solidifying billet which would cause cracking), demanded somewhat special hydraulic gear for the lowering of the billets.

DR. V. KONDIC,* B.Sc. (Member): The field which has been selected for the discussion of non-ferrous ingot melting and casting at this Symposium is limited to the metallurgical aspects of the problem. When dealing with the subject of semi- and continuous methods of ingot casting, the main interest is usually centred around the questions of technique and production. As the discussion of these two questions is outside the scope of this Symposium, I shall limit myself to a few remarks dealing with such metallurgical features of the continuous process as were not included in Bailey and Baker's valuable paper.

The metallurgical advantages of the semi-continuous methods of ingot casting are well known: high soundness, fine crystal structure, good homogeneity, and consequently good mechanical and working properties. These properties result directly from the methods of pouring, and rates and directions of solidification which are inherent in the process. Other advantages should also be mentioned, e.g. the readiness with which the process can be adapted for casting different shapes and sizes, hollow and clad ingots, or even combined with hot-working processes immediately following the solidification. All these advantages are well established, and yet it seems that there is a widely held view that there are some "catches" in these attractions, and that therefore any change from the well established batch processes to continuous methods should be made with the utmost care, as the latter processes are thought to be fraught with metallurgical difficulties which are frequently omitted in the discussion of the subject. Technique and production difficulties are approached even more cautiously. For the reasons already given, I shall confine myself to the metallurgical difficulties, which are not less complex than the technique or production difficulties. Metallurgically, semi- and continuous methods do not differ; the differences exist only on the technique and production side.

The main metallurgical difficulties which are met with in continuous-casting practice are, as already mentioned in Bailey and Baker's paper, those connected with ingot surfaces and internal and external cracking. Three types of surface defects are encountered: (a) surface roughness which may contain strings of oxides, (b) folds, and (c) exudations.

Surface roughness is caused mainly through the adhesion or sticking to the mould surface of a small piece of dross which remains there during the casting operation and causes a tear in the ingot surface. This difficulty can be readily overcome by such means as correct selection and fabrication of the mould, mould lubrication, use of immersed tundishes and metal distributors, and mould vibration.

Folds and ripples in the ingot surface can be avoided by proper control of pouring temperature, metal distribution in the mould, and the rate of cooling. For casting certain alloys, a specific mould material and finish may have to be used to ensure "wetting" of the mould surface.

Surface exudations are, as is well known, a characteristic feature in the phenomenon of inverse segregation to which certain alloy compositions are especially susceptible. When dealing with this surface defect, as indeed when dealing with any ingot surface defect, the following question must be faced at the start. Is it worth modifying the casting technique to the extent that it requires very close control approaching the standard of laboratory control, or is it better to use a more simple and straightforward technique which is suitable for industrial use, but which necessitates subsequent machining of the ingot surface? If the question of exudations is faced in this manner, then the answer to this problem is as follows. Surface exudations which are normally obtained on continuously-cast ingots can be minimized and even completely

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avoided at the expense of replacing a simple casting technique by a more complex one. As, however, for a great number of applications of non-ferrous ingots, it is customary to machine the ingot surface, surface exudations are not purposed to be completely avoided in the casting practice, but are kept at a reasonable minimum.

The cracking of ingots is perhaps the most formidable amongst the metallurgical difficulties which are met in continuous ingot casting practice. Fortunately, however, this difficulty is only serious for a comparatively few wrought alloy compositions which are known to be either hot- or cold-short. It is my firm opinion that half the trouble in this respect is due to the fact that the same or very similar casting technique is frequently adopted to cast such alloys as is usually used for more fool-proof alloys. With proper adjustment of mould material and design, and methods of pouring and cooling, most, if not all, ingot-cracking difficulties can be overcome. I hesitate to say all difficulties, because, surely, a limit must be reached in this direction, at which the advantages of the continuous method of casting for certain alloy compositions are outweighed by the disadvantages.

There remains only one more point with which I should like to conclude these remarks. The days of exaggerated claims about continuous methods of casting, which were very frequently shrouded in the unjustified veils of secrecy, are over. With the return to more normal trading conditions, use should now be made of one important conclusion, which resulted from the tumult of the war and the first post-war years. This conclusion can be summed up by saying that there are, at present, clearly defined fields of casting of non-ferrous ingots in which metallurgical as well as economic advantages of semi- and continuous methods do not as yet outweigh those of the standard batch methods of casting. But, on the other hand, it is equally true that there are such cases where the advantages are in favour of the continuous methods. The final decision on these points cannot be made without knowing all relevant data which are pertinent to any particular case. The fact, however, that the continuous methods of casting are only alternative methods of ingot casting, and are not likely to replace completely all batch methods of casting, cannot be emphasized too strongly.

AUTHORS' REPLIES.

MR. G. L. BAILEY and MR. W. A. BAKER: It is impossible to deal at all fully with the extremely interesting points that have been raised in this discussion, and all we can hope to do is to pick out certain items on which we would offer the following comments.

Mr. Campbell asked whether we had any information on the use of tundishes working in controlled atmospheres in this country. We do not know of the use of such devices in production operations, but the use of a tundish operating in a coal-gas atmosphere was recommended as a means of supplying the reducing atmosphere necessary for the casting of brass ingots, as Dr. Northcott has pointed out. The functions of a flaming dressing, namely the protection of the mould surface and the provision of a reducing atmosphere, were reproduced by the use of soot on the mould face and a coal-gas atmosphere. Excellent ingots can be made in this way, but it is a somewhat troublesome method in production, and coal gas can in any case only be used for this purpose with aluminium-free alloys such as the straight brasses.

Mr. Evans calls attention to an apparent discrepancy in our paper. The first reference, namely to the need for "pouring at a sufficiently high temperature to avoid premature solidification while the metal was in a disturbed con-

dition", referred to the need for avoiding solidification while the metal is actually washing over the mould face. If subsequently, after the ingot has risen beyond a certain point, the stream penetrates more deeply into the central part and detaches particles from the solidifying metal at some depth below the liquid surface, internal grain refinement can result without the surface layers of the metal being sufficiently disturbed to affect the surface quality of the ingot. The point, however, was not clearly made, the difference hingeing entirely on the avoidance of disturbance of the surface, even although there may be a disturbance in the centre of the ingot.

Mr. Brazener called attention to a similar point in asking how we thought the flaming mould dressing effected grain refinement. Our view has been that the flaming dressing, which actually causes turbulence at a particular point after the metal has risen above this, acts similarly to a deeply penetrating stream in that it ejects solid particles into the bulk of the melt which can subsequently act as nuclei. Clearly, if this happens one must be encountering some solidification while the metal is in a disturbed condition, and I think our real answer to Mr. Evans must be that on p. 300 the reference to premature solidification should be taken to refer not only to the surface layers but also to complete solidification of a rigid shell. If such a shell is formed while the metal is turbulent the surface will be rough.

We think Mr. Hitchcock has to some extent misunderstood our statement on p. 303 about the desirability of casting large ingots. We certainly did not intend to suggest that large ingots were not desirable, and our phrase "even though the final product may be required in short lengths" must not be taken to mean that we think there is any disadvantage in casting a large ingot and cropping to lengths afterwards. We had in mind the manufacturer with older equipment who is liable to argue that there is no point in casting a large ingot when a finished product is required in short lengths.

With regard to gas pick-up Mr. Hancock calls attention to the desirability of avoiding this rather than allowing it to occur and then trying to eliminate the gas. We agree that if it could be avoided consistently and regularly this would be the better course, but there are so many sources of gas contamination. Electric melting can, by providing the right sort of atmosphere, prevent contamination of the metal from the atmosphere. Moreover, if there is any considerable quantity of gas or water vapour charged in with the metal this will diffuse out into a suitable furnace atmosphere, and the gas content of the metal reach equilibrium with that atmosphere. If, therefore, very little deleterious gas is allowed to get into the furnace the atmosphere will be sufficiently free to allow most of the gas to escape from the metal itself. Should, however, the metal charged contain large quantities of initial gas or of water in the form, for example, of hygroscopic corrosion products, the furnace atmosphere would need to be a changing one to keep the concentration of hydrogen at the required level, and a changing furnace atmosphere is always likely to introduce water vapour in deleterious quantities from the ordinary air.

There are undoubtedly cases, such as those described by Mr. Waddington, where electric melting can be used in an almost ideal way, but for a great deal of work there is no doubt that a simple and effective degassing operation is cheaper than the provision of equipment and the adoption of procedures which completely avoid gas contamination.

Mr. Liddiard is quite correct in calling attention on p. 287 to a somewhat loose expression "the bulk of the ingot". Obviously, if a sufficiently coherent envelope of metal were formed around the casting it would as it cooled contract away from the mould wall, and it is the rigidity of this envelope to which we referred when rather unfortunately using the term "bulk of the ingot".

When we wrote on p. 289 of impurities forming grain-boundary films we

were thinking specifically of materials forming identifiable and detectable films. When we wrote our paper we considered that ductile intergranular films would allow movement of the grains relative to one another under rapid deformation, in which case the material would not show intercrystalline weakness although it might well do when slowly deformed. However, that view is now considerably modified in the light of recent work by some of our colleagues. A high-strength impurity in the form of continuous coherent intercrystalline films is unlikely to survive any marked degree of deformation of the polycrystalline aggregate unless it has also a high ductility. Mr. Liddiard's suggestion of a high-strength impurity film without ductility permitting deformation of the grains at stresses below the ultimate tensile strength of the brittle material entirely ignores the high strain which must be imposed upon this rigid network and which will ultimately, in fact at an early stage of deformation, cause a high-strength film to rupture as a result of the high specific strain thrown upon it.

Dr. Cuthbertson and Dr. Pell-Walpole refer at length to the advantages of tundish casting, particularly, we gather, to the Asarco method which is mentioned briefly on p. 307 of our paper. We do not wish to belittle the great benefits to be obtained from continuous casting, but sheer pressure of space prevented much more than references to the original publications in which these processes are described.

In conclusion there are two small points to which we would like to call attention. The first is that, as mentioned by Mr. Skript, we have not referred in our paper to the work of Dr. H. Lepp. How we came to write this paper without making any reference to the work which Lepp did we cannot explain—we can only apologize. The second point is that Professor O'Neill in criticizing the term "unidirectional freezing" as used by Mr. Ruddle quite rightly points out that one does not normally have continuous columnar crystals from one end of the ingot to the other, but on the other hand he does imply that such continuous columnar crystals must be the result of real unidirectional freezing since clearly he is taking unidirectional freezing in a literal sense. We do not feel there is any serious danger of misunderstanding as to what is normally meant by unidirectional freezing, which is surely that the freezing shall be towards the heat centre of the ingot in such a substantially single direction as to ensure complete feeding of the contraction of the metal as it solidifies. Whether the resulting crystals are columnar or equi-axial (please not "equi-axed") depends on other characteristics of the material in question.

MR. R. H. WADDINGTON: May I express appreciation for the privilege of taking part in this Symposium, and in particular I wish to thank all those who have contributed to the discussion for their interest and many kind remarks.

In reply to Professor O'Neill, refractory construction in each of the arc furnaces is as follows: three 2½-in. courses of first-quality fireclay brick are laid on the concave bottom, followed by three 2½-in. courses of burned magnesite brick. Side-wall structure to just above the metal line consists of 9 in. of fireclay brick next to the furnace shell, faced with a 9-in. course of burned magnesite brick. A monolith composed of periclase grain in a forsterite matrix is fused upon the base brick. This section, 20 in. in thickness at the centre, 16 in. at the circumference, and extended to cover the side-wall brick to the metal line, forms the working hearth which contains the 30-ton metal bath. Side-walls above the metal line are of 9-in. chemically-bonded magnesite brick with 9 in. of fireclay backing-up brick.

The roof is a dome structure of chemically-bonded magnesite brick retained by a water-cooled steel roof-ring. This is equipped with vent and openings for electrodes.

The charge slot opening is supported by a double arch of bonded magnesite

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brick, and the bottom of the slot over which the cathodes slide is constructed of specially designed silicon carbide bricks.

A working door is framed with sillimanite brick jambs and arch, with silicon carbide sill.

Furnace-bottom maintenance consists of fusion of magnesitic material to points of localized erosion. This work is normally done on a four-week schedule when the furnaces are drained for inspection.

Charge-slot and working-door refractories are replaced at 8-month intervals. Side-walls last approximately 2 years, except for periodic patching, and roofs last 1-2 years.

While on the subject of refractories, I should like to answer Mr. Campbell's question regarding "chemically-bonded" magnesite brick. This term refers to a type of unfired basic refractory in which the grains are bonded with setting material to give the brick shipping, handling, and construction strength. The brick may be laid dry, jointed with proprietary cements or a mixture of ground magnesite and linseed oil, depending upon local conditions.

Basic refractories are available in either the fired or unfired form. In the first case a hard, dense, mechanically strong brick is obtained by moulding under high pressure and burning at very high temperatures. In the latter case initial strength is provided by the chemical bond, and pressure moulding of carefully sized dead-burned magnesite grain and chrome ore. The materials used to create this bond are generally regarded as secrets of the manufacturers' art, but materials which are said to be considered or used include animal glues, salts added or precipitated in place such as magnesium sulphate, siccative oils, resins, plastics, and hydraulic cements, supplemented by small percentages of ceramic materials. The ceramic bond is developed subsequently as such brick become fired under actual service operations.

Further to Mr. Campbell's remarks relative to induction furnaces, in our case the low-frequency furnaces are used as pour hearths and not as primary melting units for pure copper. The furnace shell is lined with 4½ in. of chemically bonded magnesite brick backed up with 8 in. of fireclay brick and insulating material. The secondary-channel blocks are pre-formed by ramming an alumino-silicate grain material into a wood and steel mould. Shell linings last 4 years and channel blocks about 2 years on this service.

Mr. Harry Davies's contribution is especially pertinent. His remarks regarding the soundness of tough-pitch copper are compatible with the facts.

I also am in full accord with Mr. Davies's views regarding mould dressings, and particularly his reference to even adherence to the mould surface. In spite of much experimental work we have yet to find a satisfactory substitute for bone ash as a dressing when casting electrolytic tough-pitch copper shapes.

It may be of interest to note, however, that bone ash from different suppliers may have widely different characteristics, which often restrict the range of usage. For instance, one product has been found quite satisfactory for moulds used in casting horizontal shapes; that from another source was found to be unsatisfactory for this purpose and yet was acceptable for vertical castings.

Mr. Davies substantiates the superiority of castings produced from water-cooled moulds. His suggestions regarding super-cooling and non-coalescence of gases are of interest. The high conductivity of the mould material, of course, results in a rapid flow of heat from the mould surfaces to the mould body, from which it is borne away by the cooling water circulated through the internal channels. Proper co-ordination of mould mass, arrangement of cooling channels, temperature and quantity of cooling water all contribute towards a controlled rate of solidification, which is reflected in internal soundness of the cast shapes.

I quoted production of shapes in the form of phosphorus-deoxidized copper with residual phosphorus contents ranging from 0.007 to 0.060%. There is

substance to Mr. Davies's remarks regarding terminology, as the expression "phosphorized copper" perhaps might be more appropriately applied to the material with low residual phosphorus. Although in our process phosphorus is added to a cathode-copper melt, the metal being so treated is not oxygen-free.

Replying to Mr. Campbell, current is supplied to the low-frequency induction-heated pour hearth by means of a single-phase auto-transformer provided with taps to obtain varying voltage steps over the desired range. The selected rating is set at high and low voltage by means of jumper switches connected to magnetic contactors. These are actuated by relays energized by the recording controller connected to the lens-type Rayotube, and thus automatically control the current to the induction furnace.

DR. MAURICE COOK and MR. N. F. FLETCHER: In reply to Mr. Molineux's request for information concerning the treatment of new crucibles, these are seasoned for some time, that is, several days at least, in a warm dry atmosphere, and on the day before they are put into service they are placed in a dying coke-fired furnace at the end of the shift. Next day, while still hot, they are taken into normal service. In his levity Mr. Molineux seems to have missed the significance of the observation on the effect of iron in brasses of the alpha/beta type. The hot workability of brasses of this type with copper contents of the order of 60% is progressively impaired by increasing amounts of lead, but this effect can be offset by the addition of iron.

In solidifying the charge in a low-frequency furnace, concerning which Mr. Campbell asked for information, metal to a depth of about 6 in. above the crown is left in the furnace, for it is an essential requirement for the functioning of such a unit that a complete loop of metal is maintained in the secondary channel, and when putting a furnace temporarily out of commission by the freezing procedure referred to in the paper every precaution must be taken to ensure continuity of this loop. The bath is then carefully skimmed and covered with a substantial layer of charcoal, that is, about 12 in. deep, and the temperature raised to the point of zinc evolution for a period of 5 min. The cooling fan to the coils is switched off and 5 min. later the power supply to the furnace is cut. Solidification commences at the lowest point of the channel and shrinkage is fed from the bath above. When starting up the solidified furnace from cold the coil cooling fan is switched on and the standby load applied and maintained until the bath is molten, when normal operations are commenced. The yield of finished product, say strip or sheet, expressed as a percentage of the original ingot weight, is influenced by so many factors, of a non-metallurgical character, that although figures might be cited for particular sizes of strip rolled from ingots of certain shapes and dimensions, they would have little general significance. As Mr. Hitchcock has pointed out, the yield could be affected, for example, by the geometry of the ingot in relation to that of final products. A loss of the order of 5-10% is commonly incurred in the form of gate end or top discard from ingots. If carried out, and this will be determined by the quality of ingot surface and the surface quality required in the final rolled product, such treatments as milling or scalping might well result in a further varying loss of up to 10%, while the amount of discard resulting from such operations as shearing and trimming is a variable one largely influenced by dimensional requirements.

Mr. Brazener rightly points out that although the initial cost of water-cooled moulds is high in comparison with that of cast iron moulds, the cost per ton of metal cast is less for the former than for the latter. Grain refinement of casting by the use of flaming mould dressing is usually ascribed to turbulence caused by the volatile components burning off, while the larger grain-size associated with castings made with a non-flaming dressing may be attributable in some measure to the insulating effect of the dressing.

MR. E. J. BRADBURY and MR. P. G. TURNER: There is always a danger when describing the purely technical or administrative side of a production process and neglecting the economic factors which are often over-riding in their control, that a rather one-sided picture of the process is portrayed. That this has occurred when preparing our paper is shown by the comments of Mr. D. F. Campbell and Dr. L. Northcott. A brief explanation of certain of the relevant additional factors may be of help.

The plant described was chosen as being the most suitable for the production of reasonably large quantities of some thirty different compositions of nickel silver, often required in amounts varying from a few pounds to many tons. This demand was further complicated by the continually fluctuating composition level, often dictated by the immediate economic condition of the cutlery and other allied trades. The plant was developed and enlarged over a period of years, and the extraordinary business conditions which have existed since the war in respect of the very great demand for nickel silver may explain to Dr. Northcott the reason for the use of both coke and oil furnaces. The coke furnaces had, in fact, been in disuse for some years and were only brought back into use to deal with the temporary increase in demand which could not be catered for using only the oil-fired furnaces. The continued widespread use of coke furnaces led us to believe that it would be of value to include in our paper data concerning the technique devised by Messrs. Henry Wiggin and Co.

We are accused of "sitting on the fence" in the mixed use of water-cooled and cast iron moulds. In fact, in the paper, we stated that all strip moulds are water-cooled and that cast iron moulds are only used for wire bar and extrusion billet production. In these cases attempts have been made to use water-cooled moulds, but the dimensions of the wire-bar ingots and of the extrusion billets could not be altered as they were controlled by the subsequent processing equipment, and it was found impossible to produce a satisfactory water-cooled mould within the limits imposed.

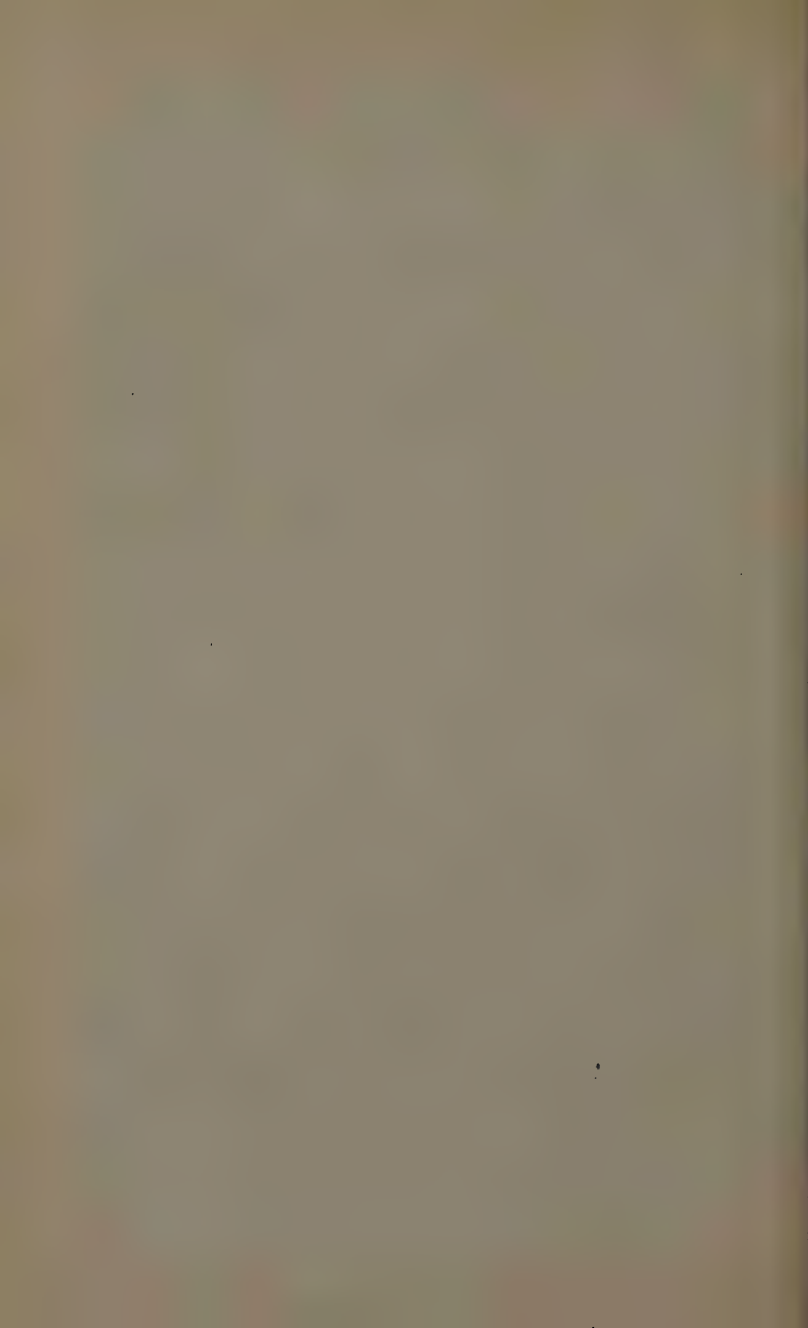
With reference to Mr. Campbell's quoted figure of 3% efficiency for coke-fired crucible furnaces, it is interesting to note that over the same period fuel costs on high-frequency furnaces, oil-fired crucible furnaces, creosote pitch-fired crucible furnaces, and coke-fired crucible furnaces, all melting nickel silver, were almost identical, the actual difference being of the order of 0.02d. per pound.

Mr. Bolton raises several interesting points. The placing of the zinc round the sides of the crucible did not, in fact, lead to increased zinc loss, but we believe that the practice inhibits the tendency of the virgin nickel to pick up carbon in the early stages of melting. It also tends to give quicker melting down owing to the swifter alloying.

Regarding the manganese and phosphor-copper additions we suggest that the manganese may check any tendency towards graphite formation, and that it also holds the sulphur.

We believe that the phosphor-copper prevents fire-cracking by enclosing the lead globules in an envelope of phosphor-copper which remains intact up to approximately 900° C., and so prevents intergranular penetration of the lead.

Finally, we would say that without going into the production costs there is no doubt that the plant fully justified itself, however "un-modern" it may appear on economic grounds. Before being closed down in 1947 it produced many thousands of tons of ingots with the necessary flexibility of manipulation to cope with requirements varying widely in respect of alloy and shape.



JOINT CORRESPONDENCE ON PAPERS BY
DR. O. KUBASCHEWSKI AND DR. A.
SCHNEIDER: "MEASUREMENTS ON THE
OXIDATION-RESISTANCE OF HIGH-MELT-
ING-POINT ALLOYS," AND BY DR. O.
KUBASCHEWSKI AND DR. H. SPEIDEL:
"OXIDATION-RESISTANCE AND SOME
PHASE RELATIONSHIPS IN THE SYSTEM
CHROMIUM-TANTALUM-NICKEL."

(*J. Inst. Metals*, this vol., pp. 403, 417.)

DR. A. H. SULLY,* M.Sc., F.Inst.P. (Member), and MR. E. A. BRANDES,† B.Sc., A.R.C.S., F.I.M. (Member): Dr. Kubaschewski and his colleagues are to be commended on a valuable contribution to our knowledge of the constitution and behaviour at elevated temperatures of some of the alloys of the high-melting-point metals. It is among alloys containing the elements listed in the introduction to the first of these papers that, in the opinion of many, the high-temperature alloys of the future are located.

There are, however, some points on which additional information may justifiably be asked for.

The first relates to the purity of the alloys which were tested and the effect of the impurities on the suggested equilibrium diagram. We note that the chromium used to prepare the alloys was electrolytic. Now Adcock,‡ as long ago as 1927, demonstrated that electrolytic chromium, as deposited, may contain as much as 1.5% chromic oxide, and this finding has been confirmed by a more recent and comprehensive investigation by Brenner, Burkhead, and Jennings§ at the U.S. National Bureau of Standards. The elimination of this oxide content is a matter of some difficulty. The authors describe four furnaces and techniques for the production of their alloys, though they do not indicate which alloys were made by each method. We submit that three of these melting procedures would result in varying degrees of purity of the chromium-rich alloys in respect of oxide content. Thus, in furnace (1), in which a hydrogen atmosphere was used, a reduction of oxide content would be expected if the hydrogen was of high purity. In furnace (2), on the other hand, in an argon atmosphere, the initial oxide content of the material would remain unchanged, while in furnace (4), in a rough vacuum of 10^{-2} mm. mercury, it is our experience that chromium can continue to oxidize at a significant rate.

These facts have an important bearing on the melting points assigned to the high-chromium alloys. The value attributed to the melting point of

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‡ F. Adcock, *J. Iron Steel Inst.*, 1927, 115, 369.

§ A. Brenner, P. Burkhead, and C. Jennings, *J. Research Nat. Bur. Stand.*, 1948, 40, 31.

chromium by Grube and Knabe * (p. 418) is misquoted, and should be $1890 \pm 10^\circ \text{C}$. Parke and Bens † give $1950^\circ \pm 50^\circ \text{C}$.

It is significant that Grube and Knabe determined the melting point of chromium containing up to 5% Cr_2O_3 and found that it was reduced to 1770° – 1790°C . The intermediate value of 1840°C . reported by the present authors strengthens the suspicion that their alloys contained some oxide.

A second point relates to the assessment of resistance to oxidation, or perhaps more correctly, resistance to the normal atmosphere, since at 1250°C . nitride formation in the high-chromium alloys is probably comparable in amount with oxide formation. The authors' tests were of short duration (100 min. maximum), and for some of the alloys it is obvious that the time is too short to permit a determination of the limiting rate of "oxidation" to be made, since the rate is still decreasing at the end of the test. Although the authors mention this point, the figures they present to show the relative "oxidation" resistance of the alloys are based on the total reduction in pressure at the end of 40 min. It appears that this procedure is capable of giving misleading information.

The criterion of most value in assessing the long-term serviceability of alloys at high temperatures is whether the scale is protective, i.e. whether or not the rate of scale thickening decreases to a negligible value. The total scale thickness is relatively unimportant, yet it is this criterion which the authors adopt in Figs. 3, 7, and 10 of the first paper and Fig. 12 of the second paper, by taking the decrease in pressure during a fixed time from the start of the test. As an example of the misleading indications which may emerge from this procedure, the case of the 40% tantalum and 40% niobium alloys in Fig. 6 of the first paper may be cited. Although inferior on the authors' basis of comparison, the 40% tantalum alloy appears to attain a negligible rate of "oxidation" after 80 min., whereas the 40% niobium alloy appears to continue at a linear rate, and if the curves are extrapolated to a duration of several hours it appears possible that they will cross, suggesting that the long-term oxidation behaviour of the tantalum alloy is superior to that of the niobium alloy.

A final minor point relates to the constitution of the chromium–niobium alloys, as disclosed by the diagrams from Debye–Scherrer films shown in Fig. 5 of the first paper. The 10% niobium alloy is shown as having a faint single diffraction line at approximately 67° , which is not present in the pattern of pure chromium. Since this appears to coincide with the strongest line of the Cr_3Nb_2 pattern, the inference may fairly be drawn that the solubility limit of niobium in chromium lies a little on the low side of 10% niobium and not between 10 and 20% as the authors suggest.

The AUTHORS (*in reply*): We are grateful to Dr. Sully and Mr. Brandes for their interest in the papers. We believe that their objections are to some extent justified, but that they do not affect the general findings in any way. The first question cannot be answered, since the oxygen content of the chromium was not determined. Recent work by Carlile, Christian, and Hume-Rothery ‡ gave the melting point of electrolytic chromium as 1836°C ., which became 1845°C . after hydrogen treatment of the metal. It would appear from a comparison of the two investigations that our chromium probably contained approximately the same amount of Cr_2O_3 as their untreated metal, namely 0.5–0.7%. This oxide content is probably to be

* G. Grube and R. Knabe, *Z. Elektrochem.*, 1936, **42**, 793.

† R. M. Parke and F. P. Bens, *A.S.T.M. Symposium on Materials for Gas Turbines*, 1946, 80.

‡ S. J. Carlile, J. W. Christian, and W. Hume-Rothery, *J. Inst. Metals*, 1949–50, **78**, 169.

found in most of the chromium-rich alloys, since the majority were prepared in furnace (2) (for removing the hydrogen in the metal). Carlile, Christian, and Hume-Rothery estimated the melting point of pure chromium to be 1860° C., Grube and Knabe's value (which was inadvertently misquoted) being possibly too high, owing to inaccurate pyrometry.

The problem of presenting and interpreting the results of the oxidation test is a difficult one when the single time-laws (parabolic, linear, or exponential) do not apply. The most satisfactory method, that of reproducing all the pressure-decrease-time diagrams, was rejected as requiring too much space. It was decided to give the rates of pressure decrease after a certain time, and to supplement these with descriptions of the nature of the "oxide" coatings. In this way it was intended to indicate which concentration ranges of the alloys were most likely to merit more detailed study. This further study should include such tests as the measurement of oxidation-resistance under repeated temperature changes. In a few instances (not mentioned in the papers) such measurements have been carried out with chromium-tantalum-nickel alloys and, though the absolute oxidation rates were different, the sequence of the alloys in the order of their oxidation-resistance was the same as in the constant-temperature tests.

Unfortunately, the observation "whether or not the rate of scale thickening decreases to a negligible value" is not alone a sufficient criterion in assessing the long-term serviceability of alloys at high temperatures. A striking illustration of this was found with the niobium-nickel alloys (p. 415). From the decrease-in-pressure curves the oxide layers appeared to become completely protective after exposure for some time. However, since these oxide layers flaked off the cooled test-pieces at a slight blow, it was concluded that during their formation the adhesion between these very dense layers and the metal was broken, owing to the high volume ratio $\text{Nb}_2\text{O}_5/2\text{Nb}$, and thus caused an interruption of diffusion, resulting in a cessation of oxidation and in the production of a mechanically weak coating. Obviously many observations must be made and considered before the protective value of the "oxide" layer can be assessed.

A simultaneous formation of oxide and nitride is very probable in our investigations, as was mentioned in the papers. At 1250° C., though CrN, for instance, is decomposed,* the dissociation pressure of Cr_2N is still low. As a rule, however, nitriding reactions are much slower than oxidation processes.† In German terminology, the difference between a pure oxidation and the possibly complex reactions taking place with exposure to air is briefly expressed by using different words. *Zundern* is used as a more general expression in place of *Oxydation*. It may be useful to introduce a new word in the English language also. Reactions in air are more complicated than in pure oxygen, but their (empirical) study is more likely to simulate actual working conditions.

* G. Valensi, *J. Chim. Phys.*, 1929, 26, 202.

† See, for instance, L. G. Carpenter and F. R. Reavell, *Metallurgia*, 1948, 39,

DISCUSSION ON THE PAPER BY MR. E. F. EMLEY: "NON-METALLIC INCLUSIONS IN MAGNESIUM-BASE ALLOYS AND THE FLUX-REFINING PROCESS."*

(*J. Inst. Metals*, this vol., p. 431.)

Dr. F. A. Fox,† F.I.M. (Member): This is an important paper, and in its own field it will clearly come to be regarded as a classic. It is the fruit of much difficult work throughout the war years, and its publication, in my opinion, does a very considerable service to the magnesium industry of the world.

Before and during the war, the fluxing of magnesium and its alloys was a subject wrapped in technical and commercial mystery. It was regarded as a key subject—perhaps *the* key subject—in the successful manipulation of the alloys, and no interested firm at that time would think of publishing its flux compositions, whether patented or not.

The publication of this paper changes all that, and the old mists have been blown away for good. Anyone who studies this paper—and it deserves study—can put himself well on the road to making his own fluxes, at least for the ordinary alloys, if he can get the materials cheaply enough.

Let us look a little more closely at the old orthodox theory of the fluxing mechanism as put forward by the pre-war pioneers, and let us consider its relation to the theories which emerge in the course of the present publication. It must be remembered that here we are dealing mainly with mechanical rather than with chemical purification. It used to be thought that a crude magnesium melt consisted essentially of metal plus more or less stable inclusions of chloride, oxide, and flux. This metal could be cleaned only by the application of some technique which would carry down these particles very much as rain clears dust from the atmosphere. The refining flux was not only inspissated but was also inspissating, and it exerted its cleaning action mainly by thickening suspended chlorides so that they were caused to settle by being made more dense.

A radically different picture is now presented. Crude magnesium melts are in fact not so crude from the point of view of oxide and flux inclusions, since these, if they are initially present, settle very readily by themselves in the right temperature ranges. If the sides and bottom of a crucible are covered with a layer of suitable inspissated flux, oxide inclusions will readily adhere to it, and will be immobilized. The essential function of an inspissated flux is not to act as a depressant but as an inclusion immobilizer and as a cover of such a kind as to permit the pouring of clean metal. Oxide and flux inclusions in the final product, if they appear, are due not to some original state of the metal but to conditions at the time of pouring, and are connected with the pouring or moulding technique.

This seems to me to be a much more satisfying picture than the earlier one, and, on the evidence in this paper, it has, I think, to be accepted. The author very rightly points to one obvious conclusion of practical importance, and that is that, if inclusion troubles arise, attention must be directed to the conditions surrounding the pouring operation, or to the moulding conditions, and

* Discussion at the Annual Autumn Meeting, Paris, 7 October 1949.

† Deputy Technical Manager, H. J. Enthoven and Sons, Ltd., London.

not to some original sin in the metal. It cannot be too often repeated that the price of good magnesium alloy castings is continued care and attention to casting detail, of which pouring itself now seems to be the most important single item.

What is puzzling is the question of how the pioneer workers came to form the earlier picture. How did it come to be supposed that a crude magnesium melt was probably loaded with stable inclusions? Beck, for example, is very specific on this point, and on p. 315 of his book * he refers to a fluxing technique in which the quantity of flux to be added must be exactly matched to the amount of oxide, nitride, and other impurities which have to be removed from the melt. Even after the invention of inspissated fluxes, and when the immobilization mechanism now put forward by the author was already in operation, it was still thought that the melts contained stable inclusions. How did this view persist, I wonder, at that time? I suppose that it is often somewhat difficult to find a convincing answer to the question of why our predecessors thought so-and-so. In this case it is not made easier by recalling that the author shows that flux and oxide inclusions settle readily even in small melts and with short times; the effects which he describes are not the result of more modern larger-scale working.

Then we have the point that settlement is markedly helped by an increase in the temperature of the melt. The earlier workers, pre-occupied with the superheating phenomenon and its applications, certainly would not have worked at too low a temperature. Incidentally, it is very agreeable to notice how various favourable temperature ranges coincide very happily for these alloys. Any temperature above 750° C. promotes rapid settlement of impurities; the hexachlorethane process of carbon grain-refinement is efficiently carried out at temperatures of this order; and the casting temperature for most sand castings of these alloys is also of the order of 750°-780° C.

On the whole, it may be that the earlier difficulties and theories were mainly connected with a lack of appreciation of the extreme care required in the pouring operation; jerky handling of the crucible, which is mentioned by the author, may have been one cause of trouble of this kind. It is clear, at any rate, that the earlier workers were often unable to distinguish between oxide and flux inclusions, and no doubt this did not help them in their analysis of the problem. The elegant methods which the author gives us in the various appendices make that difficulty a thing of the past. Anyone who has tried to prepare micrographs such as are reproduced in many of the plates in this paper will appreciate that these in themselves are also an achievement.

In one limited way the effect of this paper is to bring the theory of the flux treatment of magnesium alloys rather nearer to that of aluminium alloys. Both types of material are now seen to behave similarly while standing in the crucible, and raising the temperature leads to more rapid separation of impurities in both. For both also it is important that pouring conditions should be carefully controlled; magnesium merely has to be supplied with an artificial protection equivalent to the tough film of Al_2O_3 ; this is the refining flux cover.

There is one other point which I should like to put. This work is general in character for the magnesium-aluminium-zinc alloys. No mention, however, is made of the fact that these alloys are melted in steel crucibles. What part can the iron or the carbon be expected to play in the fluxing mechanisms? It may be that for these purposes they can be regarded as inert, though in fact they are not. Would the author care to comment on this?

As we are discussing this subject in Paris, I feel that it would not be appro-

* "The Technology of Magnesium and its Alloys." London: 1940 (F. A. Hughes and Co., Ltd.).

priate to close this contribution without referring to the classic book of Caillon on magnesium alloys which was published in 1938* and which has just appeared in revised and enlarged form.† We found it of very great value in England during the early war years, and I hope that he or his successors over here may soon be able to give the world further contributions on the same high level on magnesium alloys.

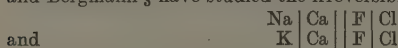
I should like to compliment the present author on the patience, experimental skill, and scientific and technical knowledge so clearly brought out in this paper, which will provide profitable reading not only for the magnesium industry but for all who deal with reactive metals.

DR. H. K. HARDY,‡ M.Sc., A.R.S.M., A.I.M. (Member): Accurate and reliable information on fluxes for the melting of magnesium-base alloys has for a long time been confined to the patent literature, but, as in the case of many other metallurgical subjects, really accurate and reliable information can be obtained from patents only by the expert in the particular subject.

It is evident, from the melting methods used in the present research, that the first essential function of an inspissated flux (p. 466, Section 4 (a)) is not to remove suspended impurities from the metal during the refining process; but, while this statement is strictly correct, it represents, I think, an over-simplification of the capabilities of an inspissated flux. It is true to say that an inspissated flux does not chase the impurities through the melt, but an inspissated flux is quite capable of collecting any impurities brought to it by convection or by the stirring of the metal. It is shown in Table II, and the matter is discussed on p. 443, that an inspissated flux seems to be more capable of gathering these particles than a fluid flux, and this effect still awaits a full explanation. The extra stickiness due to fluoride additions seems to be an unlikely cause. The magnesium fluoride is almost insoluble in the melt. Possibly the answer lies in a difference in distribution of the two sorts of flux on the walls of the crucible. The fluid flux may be expected to form a continuous, very smooth layer, while the inspissated flux may form a lumpy layer which projects slightly into the melt, and possibly the impurities are collected at the points.

On p. 443 the author mentions that more information about the wetting of magnesium oxide being promoted by magnesium chloride will be given later in the paper, but I was unable to find it, and I should like to ask for some details. The absorption of insoluble particles into a liquid layer owing to the requirements of minimum surface energy is easily illustrated by a model composed of trichlorethylene and magnesium oxide. If water is added and stirred, the magnesium oxide is absorbed into the water, leaving a clear layer of trichlorethylene floating on top. When more magnesium oxide is added, the water flux becomes very thick and pasty, and the action is probably very similar to that of an inspissated flux.

The reaction between calcium fluoride and magnesium chloride discussed in Appendix IV is interesting. Similar reactions occur in the systems sodium chloride-calcium fluoride and potassium chloride-calcium fluoride, calcium chloride being one of the end-products of the reaction. Krause and Bergmann § have studied the irreversible reciprocal systems:



* A. Caillon, "La Fusion industrielle du Magnésium et ses Moulages en Sable". Paris: 1938.

† A. Caillon, "La Fonderie des Alliages légers et ultra-légers". Paris: 1949.

‡ Physical Metallurgist, Fulmer Research Institute, Ltd., Stoke Poges, Bucks.

§ I. E. Krause and A. G. Bergmann, *Compt. rend. (Doklady) Acad. Sci. U.R.S.S.*, 1942, 35, (1), 20.

and have given liquidus surfaces for these systems. In Fig. 3 (p. 457) of the present paper we are given the quantity of calcium fluoride required to inspissate Melrasal MZ flux at different temperatures. Now, this flux contains a small quantity of magnesium chloride, which we can ignore, and otherwise it is essentially potassium and sodium chlorides with calcium chloride. If we can treat the potassium and sodium chloride together, we can use the liquidus surface given by Krause and Bergmann for the system $KCl : CaCl_2 : CaF_2$, from which we can determine the quantity of calcium fluoride soluble in the melt at different temperatures.

I have done this, and the resulting figures can be subtracted from the quantities given in Fig. 3 for the amount of calcium fluoride to inspissate the flux. The difference is, of course, the amount of calcium fluoride undissolved in the flux at these testing temperatures, and a new curve is obtained for the insoluble calcium fluoride. This is also substantially a straight line independent of temperature, with approximately 25–30% CaF_2 undissolved at all temperatures and this is of the same order as the quantities of the other inspissators.

MR. J. B. WILSON,* B.Eng., A.I.M. (Member): I think that to people who have read accounts of early experiences with magnesium alloys, and also to people who have had some very short initial experience with them, the fact that the author found such considerable difficulty in preparing magnesium alloys containing flux inclusions will come as a great surprise. I myself, over a period of years—I must confess that I was not convinced instantly by any means—have become of the opinion that it is virtually impossible to produce stable oxide and nitride inclusions in a melt of “standard” magnesium alloy. As I shall mention later, I am not quite so convinced that *relatively* stable flux inclusions cannot be prepared in these alloys.

The author has established that castings containing flux inclusions can have derived these only from flux which has flowed into the pouring stream up the side of the pot, i.e. flux which was adhering to the side of the pot, and being too fluid, has poured with the metal, or from particles which have become detached from the protective cover; or alternatively from flux which was present as an extremely thin enveloping film wetting the whole surface of the pouring system and presumably even enveloping the whole of the final casting.

On the question of whether particles of flux suspended in the metal can be made *relatively* stable or not, I wonder whether the author has fully considered the question of scale effect, particularly with respect to settling time and the relative violence of convection currents occurring with different proportions of breadth to depth of crucible and different positions of application of the furnace heat. For instance, it is possible that a furnace supplying heat to the bottom of the crucible might cause sufficiently violent convection currents to maintain particles of flux in suspension, and this might also apply to skins of oxide or nitride.

Although it may be possible to prepare initially a completely moisture-free flux, the fact that fluxes contain deliquescent materials means that in practice they invariably contain moisture. This will react with the magnesium to form hydrogen bubbles; and it seems that it should be possible to get an inclusion in a magnesium melt buoyed up, perhaps with the aid of convection currents, by hydrogen bubbles.

To me, the most interesting point in the paper is the form of porosity which is commonly referred to as “spider microporosity”, owing to the spidery appearance of a section of the cavities. If it is true that such inclu-

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sions are lined completely with a film of flux, the explanation put forward in the paper would be rather inadequate. It is very difficult to imagine that an extremely thin film which initially covers only the pouring stream would be sufficient, not only to cover the particular hot spot on the surface of the casting, but also to spread out and line these exceedingly tenuous cavities which must have very large specific surfaces.

In this connection, I should like to ask the author whether he does not think that the methods for flux detection which he has developed might not be too sensitive. My own experience of the hypo humidity chamber is that it tends to exaggerate the effects of flux inclusions, particularly those of small dimensions, entirely beyond their true practical importance. Has the author a similar impression of the test?

The final point on which I want to touch is one which I think can cause most trouble in the development and use of magnesium fluxes, namely the problem of the liquation of a fluid chloride-bearing constituent from the flux. This is clearly the mechanism which leads to the pouring of a film of flux with the casting stream, and I wonder whether the author would care to expand on the factors which determine whether fluid constituents can liquate from flux covers.

Mr. E. F. MAILLARD,* B.Sc. (Member): I am grateful that so definite a basis has now been provided for beliefs which I think are somewhat generally held in the magnesium foundry with regard to the action of fluxes, and in particular the relative lack of importance of the actual composition of the flux, provided that its physical properties are satisfactory, and the rapidity with which the flux separates from the metal. In the past it has been very difficult to insist upon matters of that kind, but I do not think that any further difficulty will now arise.

There are two points on which I wish to ask for information. The first is why the flux which is poured into the casting does not rapidly sink or rise to the surface. There is no doubt in my mind—and the author's work has definitely shown this—that flux does get into the casting by being poured in, but once it is in the mould one would expect it to separate rapidly; however, that does not happen. There are in special cases certain obvious explanations. In some cases the metal may have partly solidified, but one would expect the flux to remain in a sort of stratum in a casting. That does not happen, because we have on numerous occasions obtained flux of quite a massive sort, spread throughout the billet.

The other question is one in which I am more interested, and one which the author has regarded as rather trivial, namely the residual flux. These widely distributed particles are, on his estimate, of about 0.3 mm. dia. Nearly every magnesium casting does in fact contain flux widely disseminated in particles of that order, and for many purposes they are unimportant; but I believe that for some purposes they are of importance, as for instance in regard to the adherence of paint films.

I have thought about this matter to some extent, in relation to a second paper,† not now under discussion, in which flux difficulties of the same sort were encountered on a more distressing scale. Similar alloys made with other metals suffer from similar defects. To a first approximation, it appears that this sort of flux inclusion is always associated with the precipitation of some solid material; frequently, as in the case of the zirconium-containing alloys, with the formation of an actual precipitate due to the alloying elements, but in some cases, apparently, due to the formation of a pre-

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† *J. Inst. Metals*, this vol., p. 481.



FIG. A.—“ Fluffy ” Oxide in Magnesium. $\times 100$.

[To face p. 1110.]

cipitate caused by supersaturation. It seems that small particles, or active particles of some kind, form in the melt, attract flux to them, and retain it obstinately.

I describe this because I do not feel convinced that the application of Stokes's law to this residual flux is in fact justifiable.

MR. J. AKERLUND * (Member): The comments which I wish to make on this paper have already been covered by Dr. Fox and Mr. Wilson, but I want to take the opportunity of congratulating the author on his paper and of assuring him that it has been and is of great use to those of us who deal with the melting and casting of magnesium. I thank him for his work, and I hope that this paper will be followed by a similar one on aluminium.

DR. E. SCHEUER † (Member): What interests me in connection with this paper is not so much the magnesium part of it, because I am comparatively little interested in magnesium, but the analogy between what the author finds with regard to magnesium and the behaviour of fluxes in melting aluminium. I think that there is a considerable degree of similarity between the action of flux in magnesium and its action in aluminium, the main point being that surface energy is probably the predominant factor in all flux action in light metals. Another point is that it is not so easy to introduce magnesium oxide or aluminium oxide into the melt—not so easy as one thought before—and all the evidence that has been produced from time to time indicating the danger of oxide content, especially in a finely dispersed form, seems to be doubtful.

The AUTHOR (*in reply*): First of all, I should like to thank Dr. Fox for his kindly remarks, and for the clear exposition which he has given of the fundamental difference between the older views and the present findings concerning the mechanism of the action of an inspissated flux. I should like to quote an analogy which Dr. Fox himself mentioned on another occasion, when he likened inclusions floating in a body of molten metal to flies buzzing about in a room. According to the older ideas, you went after these flies with a "Flit" spray, but the new ideas indicate that it is sufficient to line the walls with fly-paper and in due course any flies present will collect themselves.

With regard to the origin of the earlier views, I think that it is possible to see how these arose. Before the invention of the inspissated flux, all melting was done with a protective flux. Such flux tends to collect round the edges of the metal surface in contact with the pot walls, and, despite apparently thorough cleaning of the surface of the metal, this residual flux can seep over as a thin film on the under-side of the metal stream; moreover, if a fluid flux is stirred into the melt to refine out the oxide, the sides of the crucible become coated with a layer of fluid flux which tends to pass over with the metal stream on pouring. Thus metal containing chloride inclusions was readily obtained, and, as it appeared that reasonable care to exclude surface flux had been taken in pouring, the inclusions were attributed to globules of flux suspended in the molten metal.

When the inspissated flux was invented, people tried to explain its action, perhaps naturally, on the lines of the current ideas on the subject, and when they found that flux-free metal was obtained they thought that the inspissated flux had acted as a "Flit" spray and had mopped up the

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† Chief Metallurgist and Head of Laboratories, International Alloys, Ltd., Aylesbury, Bucks.

"flies". I am sure that Dr. Fox is quite right in saying that probably insufficient attention was paid to the necessity for cleaning the metal surface adequately before pouring. That is really a very important point. In Appendix III there are some notes on how one can clean the metal surface so as to be able to pour clean metal however much a melt has been contaminated, e.g. by stirring in large quantities of oxide or fluid flux.

Dr. Fox mentioned the effect of temperature on the settling of the oxide, and that also is important; but I think that it is true to say that in all normal foundry operations where melting has been carried out with an inspissated flux, and where, therefore, the pot walls are to some extent lined with such a flux, one is not dependent mainly on settling for getting rid of the oxide, because the oxide sticks very readily to the walls of the crucible. An illustration of this—at any rate on a small scale, where admittedly the conditions are rather favourable—is given in Table I on p. 442 of the paper. The sample of oxide-contaminated metal referred to as (c) was merely poured carefully with minimum turbulence into a crucible coated with refining flux and poured straight out again, and yet the quantity of oxide in the melt, as judged by the analysis for boron, has been reduced thereby to one-tenth of what it was originally.

I am very glad that Dr. Fox has said how useful we in England have found the work on fluxes carried out by Caillon* and Hardouin,† and published in the French Air Ministry Reports before the war. These investigations were of extreme benefit, and saved me personally a great deal of time. They did, in fact, form the only potentially reliable information then available, for we found that the information given in the patents was extremely unreliable.

Dr. Hardy referred to the information summarized in Table II concerning the mopping-up of suspended oxide skins by fluxes, and said that he did not think that the magnesium fluoride would play a large part in the mopping-up process. I should explain that magnesium fluoride is not completely insoluble in magnesium and does dissolve to a sufficient extent to modify very appreciably the contact angle between the metal and the flux. In the absence of any dissolved fluoride, the contact angle appears to approach zero, the actual angle depending on the cleanliness of the surface; but with a small amount of fluoride the contact angle is very much increased. In Table V, the thirteenth column from the left gives figures of 0.8, 1.3, and 0.9% for the amount of magnesium fluoride (calculated by difference) which appears to be in solution in certain chloride mixtures. The solubility of magnesium fluoride in such mixtures appears therefore to be about 1%, and quite sufficient to cause this increase in contact angle and to confer on the flux a somewhat oily appearance and a certain degree of stickiness.

Dr. Hardy asked about the stated effect of magnesium chloride in promoting the wetting of magnesium oxide. What I had in mind—and this has some bearing on one of Mr. Wilson's questions—was that if one has a flux consisting of an insoluble infusible powder suspended in a chloride mixture which does not contain much magnesium chloride, the oxide tends not to be easily wetted by the chloride base: a layer forms on the top which is predominantly oxide, and a thin fluid layer forms at the bottom. One of the ways of overcoming such a situation is to pre-fuse the flux, making sure that all the particles of oxide are thoroughly wetted by the chlorides. Another method is to add more magnesium chloride, which can confer sufficient wetting power to avoid this "dry-top effect", as it is called. Dr. Hardy may have thought that I was referring to magnesium chloride as promoting the wetting of magnesium oxide at an oxide/metal interface,

* A. Caillon, *loc. cit.*

† M. Hardouin, *Publ. sci. tech. Ministère Air, Rapport 28, 1934.*

but actually I had in mind promoting wetting at an oxide/air interface and not at an oxide/metal interface.

Dr. Hardy also mentioned a calculation he had done which showed that the amount of calcium fluoride out of solution in the flux represented by the upper curve in Fig. 3 was about the same at all temperatures. I think that that is a very interesting calculation indeed, and it accords with the general interpretation of the phenomena of Fig. 3 given in this paper. It is interesting to note in connection with the conversion of chlorides to fluorides by double decomposition that it is possible to arrange the chlorides of the alkali and alkaline earth metals in the order of their ability to "chlorinate" a given fluoride, as follows :

Magnesium,
Calcium,
Barium,
Sodium,
Potassium.

If potassium fluoride is present in a chloride mixture, and barium chloride is added, the barium chloride will be converted to barium fluoride. On the other hand, if magnesium and barium chlorides are both present in a chloride mixture, and potassium fluoride is then added so that these two chlorides compete for the potassium fluoride, the magnesium will win. Such information can be very useful in designing fluxes and alloying agents for the introduction into magnesium of various heavy metals which cannot be easily alloyed in the metallic form. In deciding what reactions will take place in a given case, it is necessary, of course, to bear in mind the solubility of the fluoride to be formed. There are two principal factors involved : one is the thermodynamic possibility of forming the fluoride, as indicated by positions in the list above, and the other is whether or not the fluoride will be insoluble in the chloride mixture. In the case of forming magnesium fluoride by reaction between magnesium chloride and calcium fluoride, both factors are favourable; but potassium fluoride can form in preference to calcium fluoride in certain chloride mixtures, contrary to expectation, merely because the potassium fluoride is insoluble therein up to its melting point of 840°C . Above 840°C . the flux becomes fluid and non-wetting, because potassium fluoride melts and calcium fluoride is soluble in the chlorides.

A MEMBER : Can you say where aluminium comes in this series ?

MR. EMLEY : I think that aluminium is right at the top, above magnesium, but I will deal with that in my written reply.

With regard to the possibilities of producing stable suspensions of flux in metal, raised by Mr. Wilson, the only way in which I think that it might be done is to adopt either of the methods mentioned on p. 439 for producing stable suspensions of oxide and to employ an atmosphere of chlorine. If one were to do that, one would produce such a very fine chloride film on the metal that some would get transferred to the oxide without there being sufficient chloride formed to coagulate the oxide and send it to the bottom or sides of the crucible. It is worth trying.

Mr. Wilson's suggestion that if the flux was somewhat hydrated one might be able to get inclusions of chloride buoyed up by a gas bubble is very interesting. I have done some experiments with damp flux, one of which was to take a two-phase alloy such as magnesium with 8% aluminium, which has a considerable melting range, and to stir in wet flux so as to make

a homogeneous mass. This was then remelted, heated to 750° C., covered with a layer of inspissated flux, and the metal cast into a slab and examined for flux contamination. I think that there was only one experiment involved in this case, but no chloride inclusions were found in the slab. It is quite probable that one can, at any given temperature, suspend chloride inclusions in magnesium by the method which Mr. Wilson has suggested; but I think that on cooling or on further heating the density differences produced would be such that the flux would settle, as occurred in Experiment (f), p. 470, despite previous adjustment of the density of the flux to that of the metal at 800° C.

The phenomenon of "spider microporosity", to which Mr. Wilson referred and an example of which is given in Fig. 9 (Plate XLVI), seems to be of considerable interest. I think, however, that we only get the intergranular chloride layer where there is already a thin oxide film, and in no case does the chloride film appear to go completely round any one grain. In any given section, of course, it may appear that the chloride film goes completely round the grain, but if a section is taken at right angles it will be found that such grains are not completely surrounded.

With regard to the distance to which the chloride films can penetrate in the metal, I have poured chill-cast slabs in which a fluid flux was used on the metal surface and deliberately poured a metal stream which contained a thin enveloping film of flux. I found that even though the flux film is barely visible, it is still possible to get chloride sucked up into areas of outcropping microporosity to a distance of about 1 in. from the surface. The method used to produce the outcropping microporosity was to keep part of the mould wall red hot with a welding torch so that the underlying metal was the last to solidify.

Mr. Maillard raised the question, why any flux inclusions passing over into the mould at the time of pouring did not either rise to the surface or sink to the bottom. Such inclusions are produced at a metal/air interface, and these interfaces are not easily replaced by metal/oxide interfaces. You can therefore be fairly sure, I think, that the inclusions passing over have some air associated with them and will tend to keep near the surface of a body of cast metal. Often an oxide skin passing into the mould will stick on the side and wave about in the metal until the metal is solid. Where inclusions are completely wetted by metal and associated with metallic particles, as can arise in the alloys containing zirconium (see paper No. 1166*), you find, however, that the inclusions in any body of molten metal all collect towards the bottom and away from the sides. The tendency in standard alloys for inclusions to find their way to the surface layers of metal is well illustrated by the practicability of salvaging fluxy billets by machining off the surface layers of metal, a practice occasionally employed in the early days.

The AUTHOR (*in further, written, reply*): Dr. Fox raised the question as to what part iron and carbon derived from the usual mild-steel crucibles may play in the refining of magnesium. Iron which is dissolved in magnesium will not be affected by fluxing processes, and it appears from work referred to elsewhere† that very little removal of undissolved particles of iron or iron-rich alloys can be achieved in this way. The removal of metallic impurities from magnesium alloys, though lying outside the scope of the paper under discussion, is a subject of considerable interest, and one which it is hoped it may be possible to discuss on another occasion.

* *J. Inst. Metals*, this vol., p. 481.

† E. F. Emley, *Inst. Min. Met.: Symposium on Refining of Non-Ferrous Metals*, Preprint No. 12, 1949.

So far as is known, carbon is insoluble or practically so in magnesium, and it might be expected that suspended carbon or magnesium carbide particles would be removed by fluxing. In the presence of aluminium the solubility of carbon appears to be sufficient to initiate the crystallization of temperature-dependent hexagonal phases which can cause grain refinement.* In alloys containing zirconium, however, any carbon is likely to be present as an insoluble interstitial carbide with metallic properties, and thus, like the nitride ZrN , be unaffected by fluxing.

With regard to the position of aluminium in the series of metals representing the power of their chlorides to "chlorinate" a fluoride by double decomposition, calculations indicate that aluminium lies close to magnesium and above the alkali and alkaline earth metals.

Mr. Maillard raised an interesting point about the traces of residual chloride present in commercial alloys. He appears to me to have a much exaggerated idea of the nature and frequency of occurrence of corrosion spots due to residual chloride. These are so small that their detection even on cast metal requires the special machining technique and the special precautions to avoid dust contamination described in Appendix V. After metal has been worked, residual chloride cannot be detected even in this way. It is certain that the minute traces of chlorides referred to have no effect on corrosion-resistance, and it is unlikely that they can affect the quality of protective coatings subsequently applied, since their removal would be effected during the preliminary cleaning treatments. Of more importance is likely to be the question of subsequent external contamination from chloride-containing dust (see Fig. 19, Plate XLVIII) or contact with surfaces on which traces of chloride may be present. Incidentally, there is no evidence that manganese particles can *pick up flux* even in traces. In the paper, Stokes's law is applied to a hypothetical case, namely, to a dispersion of globules of protective flux. Its application to the settling of flux associated with particles or skins would, as Mr. Maillard points out, be unjustified.

It is interesting to note from Dr. Scheuer's remarks that it is difficult to suspend oxide in aluminium also. Unsuccessful attempts to prepare such suspensions in aluminium-magnesium alloys were made some years ago at Clifton Junction in connection with the development of fluxes for these alloys. I think that the phenomena of "fluffy" and "heavy" oxides occur also in magnesium. "Fluffy" oxide would be oxide incompletely wetted by metal and characterized by voids and metal/air interface skins (see Fig. A, Plate CXXX), while "heavy oxide" would be that formed wholly in the metal phase adjacent to metal/air interfaces (Fig. 26, Plate L), which readily sinks through the metal (Fig. 17, Plate XLVIII) and is frequently quite massive in habit (Fig. 24, Plate XLIX).

With further reference to a point raised by Dr. Hardy, the flux coatings on the crucibles used for the melts set out in Table II were applied by filling the crucibles with molten flux and draining. Even with inspissated fluxes the adherent layers appeared very smooth and uniform. Nevertheless, flux distribution on the walls of crucibles is irregular in practice, and this may well assist in oxide removal.

* C. E. Nelson, *Trans. Amer. Found. Soc.*, 1948, 56, 1.

CORRESPONDENCE ON THE PAPER BY MR.
N. S. BROMMELLE AND MR. H. W. L.
PHILLIPS: "THE CONSTITUTION OF
ALUMINIUM-COPPER-MAGNESIUM AL-
LOYS."

(*J. Inst. Metals*, this vol., p. 529.)

DR. D. J. STRAWBRIDGE,* M.A., B.Sc. (Member): I was interested to read this paper and to see how the constitutional diagrams for the slowly solidified alloys compared with the equilibrium diagrams with which I was formerly concerned.

In their historical survey, the authors refer to phases discovered or confirmed by work at Oxford,† and I feel that in some of these cases our views have not been described quite correctly, so that the following notes may be useful. The phases and formulæ to which I shall refer are shown in Fig. A, the phase fields in which are based on our 460° C. isothermal diagram. Of the five compounds shown in Table III of the authors' paper (p. 537), the *S* and *M* phases were identified as Al_2CuMg and AlCuMg , respectively, in the papers that have been cited,† but I feel that some further comment might be made with regard to the other three formulæ.

The Z Phase ($\text{Al}_{10}\text{Cu}_7\text{Mg}_3$).—Little, Hume-Rothery, and Raynor reported that the composition of the *Z* phase was "somewhere in the region suggested by Laves and Witte", but in the later paper (Strawbridge, Hume-Rothery, and Little) it was shown that this phase must contain somewhat more copper than is indicated by the formula $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$, and the view was expressed that the electron concentration of this phase (isomorphous with MgZn_5) might be much nearer to 2 than previously indicated. Fig. 9 of that paper shows the region of homogeneous *Z* to be well away from the composition of Laves and Witte's formula, in which region of composition three-phase alloys were found. A footnote (p. 200 of the paper) gave the point of intersection of the lines representing a ratio of 1 large : 5 small atoms, and an electron concentration of 2, as about 65.6% copper and 8.6% magnesium. I regret that these figures are in error, the correct values being 63.4% copper and 9.7% magnesium, corresponding, of course, to the formula $\text{Al}_5\text{Cu}_5\text{Mg}_2$. Guertler and Rassmann ‡ (to whose work the authors refer) obtained a homogeneous alloy with 60% copper and 10% magnesium, which fits in with our results, and their formula was $\text{Al}_{11}\text{Cu}_{11}\text{Mg}_4$. The composition corresponding to this formula is very near to that of $\text{Al}_5\text{Cu}_5\text{Mg}_2$. The Laves and Witte formula requires 56.5% copper and 9.3% magnesium. It is interesting to note that, of our Al-Cu-Mg-Zn alloys containing 6% zinc, those with compositions on a line in the isothermal diagram from MgZn_5 to $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$ were three-phase, but the line joining MgZn_5 to $\text{Al}_5\text{Cu}_5\text{Mg}_2$ cuts the 6% zinc section in the

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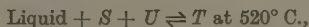
† A. T. Little, W. Hume-Rothery, and G. V. Raynor, *J. Inst. Metals*, 1944, 70, 491.

D. J. Strawbridge, W. Hume-Rothery, and A. T. Little, *J. Inst. Metals*, 1948, 74, 191.

‡ *Metallwirtschaft*, 1943, 22, 34.

region tentatively indicated in our paper (Fig. 15) as corresponding to homogeneous quaternary Z . (The validity of the argument implied here is to some extent borne out by our discovery of a homogeneous quaternary M alloy containing 6% zinc, with a composition on the line from $MgZn_2$ to M_{AlCuMg} .) I feel that our work offers more support for the formula $Al_{11}Cu_{11}Mg_4$ (or $Al_5Cu_5Mg_2$) than for $Al_{10}Cu_7Mg_3$.

The U Phase and the Y Phase.—The phase U was stated by Urazov and Petrov* to have a composition corresponding to the formula $Al_2Cu_4Mg_3$ and to be involved in the reaction:



the liquid containing 15% copper and 34% magnesium. Petrov and Berg†

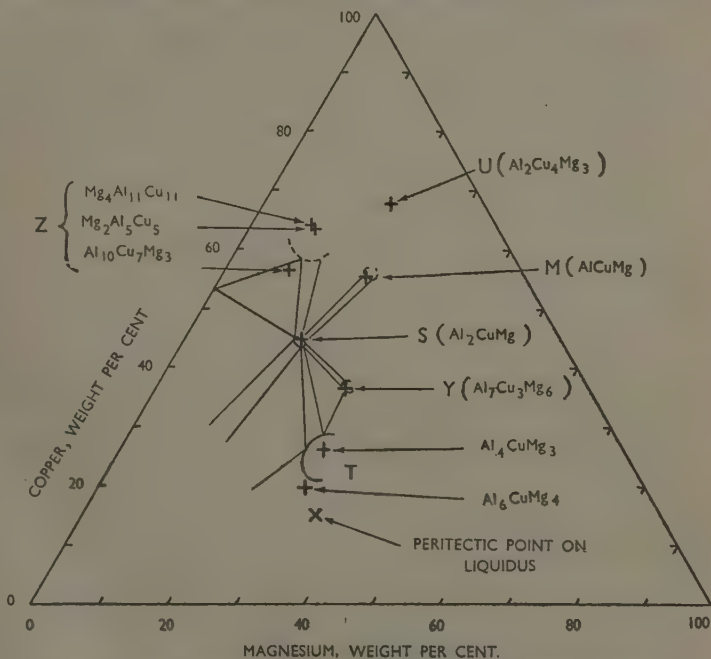


FIG. A.—Some Features of the System Aluminium-Copper-Magnesium.

published a diagram based on an examination of alloys of composition near that of S and T , and on the reports of previous workers, showing a field ($U + S + T$) beyond the ($S + T$) field. We reported a phase Y at 460°C. , corresponding to a formula $Al_7Cu_3Mg_6$, and found phase fields involving Y where Petrov and Berg reported $U + S + T$. We made no claim, however,

* *Zhur. Fiz. Khim.*, 1946, 20, 387.

† *Ibid.*, p. 1475.

that Y was the U phase of the Russian investigators. The diagram of Petrov and Berg omits the M phase (AlCuMg), and Urazov and Petrov state that it does not seem to exist; might it not be that M and U are the same phase? If one defines U as the phase concerned in the peritectic reaction, then it may be that our Y is U , as the authors have stated, but a compound corresponding to $\text{Al}_2\text{Cu}_4\text{Mg}_3$ may or may not exist as well. The geometric conditions required for the peritectic reaction do not help here, for a region of homogeneous T lies within the triangle formed by the other phases whether U be $\text{Al}_2\text{Cu}_4\text{Mg}_3$, M , or Y .

The T Phase.—The generally accepted formula Al_6CuMg_4 corresponds more nearly, in ratio of large to small atoms, than Nishimura's Al_5CuMg_4 , to the isomorphous T_{AlMgZn} (cf. Little, Hume-Rothery, and Raynor, *loc. cit.*). It is interesting to note, however, that the composition corresponding to Al_6CuMg_4 lies outside the range of homogeneous T alloys, whereas a formula which fits very well with the micrographic evidence is Al_4CuMg_3 , and this has the 3 large : 5 small atom ratio characteristic of T_{AlMgZn} . One may also note that Al_4CuMg_3 lies within the triangle formed by the reactants in the peritectic reaction referred to above, but Al_6CuMg_4 falls outside—if one accepts Urazov's composition for the point on the liquidus. It is also interesting that a product $[\text{Cu}] \times [\text{Mg}]^3$ is as compatible as $[\text{Cu}] \times [\text{Mg}]^4$ with the data given by the authors on p. 553, regarding the $\text{Al}/(\text{Al} + T)$ boundary, and, in Fig. 4, the slope of the isothermals of primary T separation corresponds more nearly to 1 : 3 than to 1 : 4.

The AUTHORS (*in reply*): We are much indebted to Dr. Strawbridge for his amplification of our discussion of the formulæ to be assigned to the ternary constituents of this system. As we emphasized in the introductory portion of our paper, we were chiefly interested in the alloys in which aluminium is primary, and as our exploration of the adjacent primary phase fields was limited, we have no first-hand data on which to base any comments on Dr. Strawbridge's contribution.

In our survey, we gave $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$ as the best-authenticated formula for the phase Z , and referred to the work of the Oxford School as supporting it. In the earlier paper by Little, Hume-Rothery, and Raynor, this formula is quoted without its validity being questioned. The composition to which it corresponds lies within the field of homogeneous Z given in Fig. 4 of their paper, and the formula is used to explain the isomorphism between Z and the binary body MgZn_5 (or $\text{Mg}_2\text{Zn}_{11}$). It is true that in the second paper, of which Dr. Strawbridge is a part author, it is stated that Z must contain more copper than is indicated by $\text{Al}_{10}\text{Cu}_7\text{Mg}_3$, and we regret that we omitted to mention this in our summary. There is, however, no suggestion in this paper that a different formula should be adopted, and we inferred that the authors regarded Z as one of those constituents having a homogeneity range which does not include the composition corresponding to the formula. Pending X-ray data on the number and arrangement of the atoms within the unit cell, Dr. Strawbridge's suggestion of the formula $\text{Al}_5\text{Cu}_5\text{Mg}_2$ might perhaps be adopted. Compared with his alternative suggestion of $\text{Al}_{11}\text{Cu}_{11}\text{Mg}_4$, it possesses the merit of simplicity, having a simple electron : atom ratio of 2 : 1, and a simple ratio of 1 large : 5 small atoms. Whether this composition lies within the homogeneity range of Z remains to be established, but this is surely a minor point.

Our reasons for thinking that the Oxford School favoured the formula Al_6CuMg_4 for the constituent T were similar. In both papers the formula is quoted, and its ratio of 21 small : 12 large atoms is claimed to be sufficiently near to the 5 : 3 ratio of the constituent $\text{Al}_2\text{Mg}_3\text{Zn}_3$ of the Al-Mg-Zn system

to account for the isomorphism between the two phases. Although the composition corresponding to Al_6CuMg_4 lies just outside the homogeneity range of T , there is no suggestion in either paper that another formula would be more appropriate. Dr. Strawbridge now appears to favour the adoption of Al_4CuMg_3 , and points out that this formula is consistent with our work on the solubility product along the $\text{Al}-T$ valley and with the slopes of the primary T isothermals given in Fig. 4 of our paper. This argument must be used with considerable reserve. The method for finding the position of the $\text{Al}-T$ boundary was not of high accuracy, and our exploration of the isothermals of the T field was limited. If Fig. 4 is taken at its face value, it can be argued that the ratio of $\text{Cu} : \text{Mg}$ atoms in T changes with temperature, approaching 1 : 4 at low temperatures and 1 : 2 at high, so that no single formula is appropriate. We suggest that the only valid reason for preferring Al_4CuMg_3 to Al_6CuMg_4 is that it has exactly the required 5 small : 3 large atom ratio.

There is clearly some uncertainty about the relationship between the phase designated U by Petrov and his colleagues and that designated Y by the Oxford School, and perhaps our assumption of their identity should have been more guarded.

JOINT DISCUSSION ON PAPER BY MR. G. R. WILMS AND DR. W. A. WOOD: "MECHANISM OF CREEP IN METALS," AND ON PAPER BY DR. W. A. WOOD AND MR. W. A. RACHINGER: "CRYSTALLITE THEORY OF STRENGTH OF MATERIALS." *

(*J. Inst. Metals*, this vol., pp. 693, 571.)

PROFESSOR J. N. GREENWOOD,† D.Sc., M.Met.E. (Member), who, in the absence of the authors, presented both papers, said: It gives me peculiar pleasure to be able to present these papers on behalf of my colleagues, because this is the first meeting of the Institute of Metals which I have been able to attend since the Autumn Meeting in 1932. I propose to read a statement by Dr. Wood, because in that way I can best give you the views which he would himself put before you were he able to be present. He writes:

Both papers virtually state that as a result of plastic deformation the grains of a polycrystalline metal develop a sub-structure which is a function of the temperature and rate of deformation and which, once produced, largely determines the mechanical strength.

We should like to emphasize the following points:

Paper by Wood and Rachinger.

First, with regard to the sub-structure associated with cold deformation at the usual rates of straining dealt with in the paper, it should be made quite clear that the prime evidence is not based on the radial broadening of X-ray lines. The basic evidence is the peripheral spread of the X-ray reflections from the sharp spots characteristic of the annealed metal to the long arcs along the diffraction ring characteristic of the cold-worked metal. This spread proves that the internal structure of the grain becomes disoriented. We then consider that in practice the disorientation under appropriate conditions of deformation can become far too large to be explained by the bending of lattice planes, though, of course, it may be preceded by bending. The only alternative to bending is a disorientation formed by dissociation into a sub-structure.

The radial broadening only comes in because, first, the limited broadening obtainable in practice places a lower limit to the size of the sub-structure and, second, under favourable conditions it may permit an absolute estimation of this limiting crystallite size. In connection with the latter point, long experience has led me to conclude that if the broadening is due partly to small crystallite size and partly to lattice strains, as it will be in the general case, it is difficult to separate the effects. I believe that the only practicable method is to try to eliminate the lattice strains experimentally, and that was the point of the experimental approach employed in the paper.

In particular, we have tried to utilize the directionality of the lattice strains often exhibited by systematically deformed metals. We consider the practice of using filings, commonly adopted by English workers, unsatisfactory,

* Discussion at the Annual Autumn Meeting, Paris, 7 October 1949.

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because it superposes an overwhelming broadening of the X-ray lines due to the random arrangement of the internal strains. It will save confusion if this distinction is borne in mind when results from various laboratories are compared.

In regard to the relating of the sub-structure to the strength, there are, of course, a number of theories, and the one followed here is basically similar to that put forward some years ago by Sir Lawrence Bragg. The additional point submitted, however, is the suggestion that more attention might be paid to the influence of the crystallite and grain boundaries in determining whether a slip movement in one crystallite can be accommodated by its neighbours.

Paper by Wilms and Wood.

In this paper the evidence for a sub-structure is overwhelming. The break-up of the initial X-ray reflection spots to groups of spots permits of only the one interpretation. In recent years interest in these sub-structures has been revived, largely because of the beautiful techniques developed by the French workers, Lacombe, Beaujard, Guinier, and Crussard. It may be of interest, therefore, to point out the similarity of, and at the same time the difference between, our results and those of other workers.

The difference is simplified by distinguishing between sub-structures in annealed grains and sub-structures developed in deformed grains.

In annealed grains or single crystals, a mosaic structure has long been established by the early X-ray work of Darwin and Bragg; the characteristics are a relative tilt of the elements from a few seconds to a few minutes of arc according to the degree of imperfection, and an approximate size of 10^{-4} cm. However, this sub-structure is believed to be essentially an accidental feature of the growth of the crystals from solution or from the melt. Lacombe and Beaujard, using chemical methods, which are less sensitive than the X-ray method, have also proved the existence of sub-structures in large annealed grains. But the size, according to published photographs, is of the order of the actual grain-size itself used in our work. It is difficult to see any relation between these sub-structures and the ones studied in the present paper, which are a systematic function of deformation conditions.

In deformed grains, sub-structures have been observed after recovery, that is, by heating before recrystallization; and these sub-structures, as shown by Crussard, produce spotted X-ray reflection arcs at first sight not dissimilar to those shown in the present paper to arise during slow deformation. In discussing these it will save confusion to remember that in practice the term "recovery" refers to recovery from relatively rapid deformation applied at room temperature, which may be shortened to "recovery from cold deformation".

A question to be answered, then, is whether the sub-structure formed after heating a cold-worked specimen to a given temperature is the same as that formed by actually deforming the specimen at that temperature. The answer, from later experimental work on points such as these, is negative. The effect of heating the cold-worked specimen is merely to clear away internal strains and distortions and reveal more clearly in the X-ray photograph the sub-structure formed by the low-temperature deformation. There may be a little growth of the sub-structure before recrystallization on prolonged heating or heating at higher temperatures, but the increase is found to be insignificant. The important point is that the sub-structure is related rather to the initial temperature of deformation than to the temperature of subsequent heating. Therefore, we regard the sub-structures noted in recovery from cold deformation at most as a very special case of the sub-structures investigated in our work; for this work shows that the sub-structure increases systematically in

size as the temperature of deformation is increased and the rate of deformation at any one temperature is decreased.

Sub-structures are formed also in hot-worked metals. The further question might be raised of whether these are the same as those studied in the paper. The answer again is that they might be considered to be a very special case, being typical of relatively rapid deformation at the temperature of working. Subsequent prolonged heating at the same or higher temperature, as before, produces no really significant variation before recrystallization. The structure again is related rather to the initial conditions of deformation than to subsequent heat-treatments; therefore it is impossible in this way to reproduce the sub-structures associated with creep because of the difference in the rate of strain factor.

Since doing this work the authors have been asked whether the effects are not just recovery effects. The answer lies in how recovery is defined, and in view of this work it will be advisable in future to distinguish between "recovery from cold deformation", "recovery from hot deformation", and "recovery from rapid or slow deformation".

DR. A. H. SULLY,* M.Sc. (Member): The work described in the first paper is of such quality that one must congratulate the authors on a notable contribution to our knowledge of the process of creep at high temperatures. One may divide the discussion into two parts; firstly, the observation of what the authors term "cell" formation, and, secondly, the part that the "cells" play in the deformation of the aggregate.

I was interested to hear Professor Greenwood speculate on the correlation between the cells which are observed by the authors and the sub-grain structure which has been observed in aluminium by Lacombe and Beaujard.† The similarity between these structures is unfortunately not mentioned in the paper, but it is obviously a point which is going to be dealt with at considerable length in the present discussion. It is tempting to regard these two formations as being identical. In the experiments of Lacombe and Beaujard the sub-structure, the macro-mosaic structure, was produced in material which had been lightly cold worked and subsequently annealed. The results of the present authors suggest that this structure may also be produced by the combination of slight strain and elevated temperature when applied concurrently, as well as when applied consecutively. There may be, as Professor Greenwood suggests, some minor differences in the formation of these macro-mosaic aggregates, but it would be extremely odd if they were not fundamentally the same type of structure.

It is significant to notice certain correlations between the observations of Lacombe and Beaujard and those of the present authors. There are the small differences of orientation between neighbouring units, only 15-30 minutes of arc according to Lacombe and Beaujard, and less than 1° according to the present authors. The number of such macro-mosaic units to each grain would appear from the photographs illustrating Lacombe and Beaujard's work to be about 10-100, which agrees fairly well with the authors' estimate of 10-20. The distinction between these "macro-mosaic" or "cell" boundaries and normal grain boundaries is probably only one of degree, the transitional lattice across the cell boundary being relatively less disordered than that at the grain boundary because of the smaller difference in orientation across the former.

Now, there is already adequate evidence to show that at a high temperature the grain boundary can show viscous behaviour, and that deformation at such

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† *J. Inst. Metals*, 1948, 74, 1.

temperatures, especially at slow rates of strain, is accompanied by relative movements of the grains at the grain boundaries and by an absence of detectable slip in the grains. This was made clear by the pioneer investigation of the metallography of creep by Hanson and Wheeler* to which the authors refer. Further convincing evidence of the viscous behaviour of the grain boundary under such conditions has also been obtained by Kê† and other workers. The viscosity of the boundary is a measure of its divergence from the regularity of the perfect metallic lattice, and since the cell boundaries may also be regarded as regions of divergence from regularity it is reasonable to predict that the cell boundaries may also show viscous behaviour under the same conditions as those in which the grain boundaries behave viscously. However, since the change of orientation is less across the cell boundary than across the grain boundary, the resistance to flow would be greater in the case of the cell boundary. This would accord with predictions which have been made by Mott,‡ that the boundary flow will depend upon the relative proportions of area of relatively good and relatively bad fit at the boundaries. Thus, under conditions of stress and temperature favourable to this mechanism of deformation, it is to be expected that deformation will be accompanied by appreciable movements at and adjacent to the boundaries, with smaller movements at the cell boundaries, and these expectations appear to be borne out by the authors' findings.

It may be noted that in Figs. 2 (Plate XCIV) and 6*m* (Plate XCVI) of Wilms and Wood's paper, of specimens in which cell formation is clearly visible, the deformation at the cell boundaries is clearly less than in the grain boundaries. It may also be inferred from Fig. 9*m* (Plate XCVII) of a specimen strained much more slowly than the other specimens, that as the rate of strain decreases most of the movement takes place at grain rather than at cell boundaries. It is particularly interesting to note that this photograph also clearly indicates that movement is much greater in some boundaries than in others orientated similarly to the applied stress. This also tends to confirm that the relative movement due to grain-boundary viscosity effects is a function of the change in orientation on traversing the boundary.

There is one point on which it seems that the authors have over-estimated the importance of the cell structure. This is on the last page of the paper, where the statement is made that "but for the possibility of the internal deformation by relative movements of the sub-structure, the metal would quickly part at the grain boundaries and so fracture". At very slow creep rates, deformation can occur to an appreciable extent by relative movement at the boundaries, accompanied by localized deformation in those regions of the grains near the boundaries where stress concentrations exist due to the interlocking of grains. The apparent widening of the boundaries, shown so well by Hanson and Wheeler (*loc. cit.*), is illustrative of such localized deformations. Under these conditions, it is true, fracture normally occurs with much less total deformation than in normal tensile tests at the same temperature, but it is not necessary to postulate a sub-structure to account for the fact that a limited creep deformation can occur.

It is to be hoped that the authors will be encouraged to extend their observations to metallic single crystals, where the effect of the cell structure can be studied independently of the complicating effects of the grain boundaries. Under these conditions Hanson and Wheeler's work suggests that, irrespective of the temperature or the rate of deformation, the deformation is always accompanied by normal slip processes. It would, however, be most valuable

* *J. Inst. Metals*, 1931, 45, 229.

† *Phys. Rev.*, 1947, [ii], 71, 533; 72, 41.

‡ *Proc. Phys. Soc.*, 1948, 60, 391.

to confirm whether this is so or whether there are conditions in which the quasi-viscous (or secondary) component of creep is accompanied only by localized distortion at and near the sub-grain boundaries. It is also to be hoped that the authors will accompany their observations with deformation-time curves, since a correlation of their observations with various stages of the creep curve, particularly with the accelerating stage of creep immediately preceding fracture, would be of very great value to all interested in the mechanism of slow deformation.

MR. R. J. L. EBORALL,* M.A. (Member): Many of us have seen at first hand in the last few days some of the recent French work on the formation of sub-grain structures, and I think that we are well on the way to obtaining a good understanding of how these structures are formed, and some idea of what their importance may be. The paper by Wilms and Wood is an important contribution to this body of knowledge, and particularly to a knowledge of what happens in hot deformation at slow rates. It may be that the kind of change which they have found is common to other conditions of hot deformation, and it will be interesting to see whether this turns out to be so.

I should like to confine myself to the question of whether the sub-structures which are developed in creep are of the same type as the sub-structures which the authors propose for the cold-worked metal. One enters with some hesitation on a discussion of the subject of line-broadening; but I think it is fairly safe to say that Wood and Rachinger have proved their contention that particle-size broadening is present in cold-worked metals. It is interesting that they have also conceded the point that in most of the experiments which have been done by other workers line-broadening due to randomly-oriented stresses predominates, and that it has become apparent that the difference here is that in massive metal deformed in certain ways the randomly-oriented stresses may not be very large. It would be of great interest to see whether these observations could be extended to other metals, especially those of the face-centred cubic type.

Now, if particle-size broadening is present, it might appear that fragmentation into small "crystallites" of the type which the authors postulate does take place, but I think there is no proof of that, and the observations are equally well interpreted in terms of severely distorted lattices. The real observation which has been made is that the quantity of metal which behaves as a unit in diffraction is small, and nothing can be said about whether those units are continuous with one another in a curved lattice or have sharply-defined boundaries between them.

In this paper there is a statement to the effect that the diffraction effects observed are similar to those from a shattered mirror, and that a shattered mirror gives reflections over a continuous range of angles. That is true if the shattering is to a fine enough size, so that one cannot see distinctly the separate images in each part of the mirror; but if it is possible to have a method of high resolution it should be possible to see those distinct images, and therefore to say whether or not the mirror is bent or shattered.

There is a good deal of evidence now, especially from the work of Cahn † and of Guinier, Tennevin, and Lacombe ‡ that a deformed crystal is continuously bent, and that discrete perfect blocks of quite large size are formed by the subsequent local straightening of the bent lattice ("polygonization"). These observations, it is true, have been on coarse-grained or single-crystal materials. At the B.N.F.M.R.A., we have been studying similar changes in

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† R. W. Cahn, *Phys. Soc. : Rep. Conf. on Strength of Solids*, 1948, 136.

‡ A. Guinier and J. Tennevin, *Compt. rend.*, 1948, 226, 1530.

A. Guinier and P. Lacombe, *Métaux et Corrosion*, 1948, 23, 212.

fine-grained materials, and our observations agree in kind with those of the French workers and of Cahn. For small or moderate deformations we can find no evidence that the cold-worked metal is broken up into distinct "crystallites" before the application of heat. The formation of perfect blocks is a second process, and they are much larger than 10^{-6} cm. I think that this question would bear a good deal of further investigation, but the evidence which is being put forward now can be fitted quite well into a more or less self-consistent picture of what happens on cold working and annealing before recrystallization.

PROFESSOR C. CRUSSARD *: My remarks will be confined almost entirely to the paper by Wilms and Wood, and I shall make only a few comments on the second paper. The subject of the first paper is so important that it deserves very careful examination, both from the experimental and from the theoretical point of view.

I should like to begin by mentioning an historical point. The dividing of crystals into sub-grains—I use the word "sub-grain" because it seems to me that it does not imply any interpretation of the phenomenon observed—during creep was first observed by X-rays by Homès,† in Belgium, and by micrography by Jenkins and Mellor‡ in steel.

At the Ecole des Mines, we have observed the same phenomena, and I published a paper three years ago on the subject of the fragmentation of crystals during creep at 200° C. of highly refined aluminium.§ We have also examined metals such as zinc and magnesium, and have observed that in these metals the fragmentation or formation of sub-grains is much more difficult than in face-centred cubic metals, if not almost impossible. This is due to the different behaviour with regard to slip mechanism and the number of possible slip planes. We have carried the work a little further, and, using a very fine focus on the target of the X-ray apparatus, we have obtained a better resolution which enables us to see that even in a metal deformed at room temperature a kind of division into sub-grains takes place. In such cases, of course, the sub-grains are not at all as perfect as they are when produced at higher temperatures, and they still have some internal strains.

We have observed that the purer the metal the coarser the sub-grains, so that the purity of the metal is a very important factor. We have also observed the formation of coarse sub-grains in single crystals of aluminium extended at room temperature, || and in single crystals elongated by creep at about 200° C.

We have been convinced by these experiments that in the case of the single crystals there is a relationship between the formation of sub-grains or cells and the formation of deformation bands or "kinks", as Dr. Orowan calls them; so that the observations which we made led us to a different interpretation from that proposed by the present authors. It seems to me to be obvious that the formation of cells or sub-grains is identical with polygonization. As a matter of fact, the X-ray diagrams which we obtained after creep at 200° C. were exactly the same as the ones which we had obtained after cold working and annealing at a higher temperature. We shall deal later with the question of why we have to anneal at a higher temperature to observe the same pattern.

Moreover, I think that it is impossible to regard these sub-grains as being formed and tilted relative to one another by some kind of viscous movement, because this would imply a diffusion of atoms along the boundary between the cells over enormous distances, a process which seems to me to be highly

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† *Rev. Mét.*, 1939, **36**, 373.

‡ *J. Iron Steel Inst.*, 1935, **132**, 179 P.

§ *Rev. Mét.*, 1946, **43**, 307.

|| *Rev. univ. Mines* (Congrès A.I.Lg., Section Métallurgie physique), 1947, **41**.

improbable. It should be mentioned here that boundaries between sub-grains which consist mainly of walls of dislocation move much more easily normal to their plane than tangentially to it, so that the movement of the boundary between cells is quite different from the viscous creep at the boundaries between grains. This confirms the fact observed by Lacombe, that intracrystalline boundaries are different from intergranular boundaries.

We have observed boundaries between sub-grains in aluminium electro-polished before creep. They seem more numerous if one puts the microscope out of focus, but this is an optical illusion which makes shallow valleys on the surface appear like sharp boundaries. When boundaries are to be observed on well-focused specimens, if slip-lines are present they always cross the boundaries without interruption or deviation. Thus, there is no relative movement of the sub-grains at the boundaries.

Our observations show that there is a continuous transition between the low-temperature type of deformation and the high-temperature one. I think that this is readily explained by the theory of dislocations, as it has been developed, mainly in England, in recent years. Dislocations show two trends during their movement. If the motion of the dislocations is fast through the crystal, they can multiply by some kind of avalanche process, as suggested by Frank and myself, and in this case the dislocations will lead to the formation of strong slip bands, visible under the microscope. If they are slow, they arrange themselves in another pattern, because there is an inherent trend of the dislocations to cluster in walls. This pattern has a lower energy than dislocations randomly distributed in the metal. If you go fast you have the tendency to develop well-defined slip bands, and if you go slow you have the arrangement of dislocations into walls between sub-grains. Both processes will compete during the deformation, the former, the fast one, being prevalent at low temperature and the latter being predominant at high temperature. Going from the first case to the second leads to a progressive coarsening of the sub-structure.

There is one point which is not yet quite clear. The formation of sub-grains involves some kind of kink or deformation band, the exact role of which is not yet understood. The higher the temperature or the purer the metal, the wider will be the spacing of the slip bands, and also the wider the spacing of the deformation bands and kinks in the metal. We have observed and stated that at 200° C. the slip bands in aluminium ran not along the (111) planes but along the (110) planes, and were very coarse. I must confess that I am not sure that they were actual slip bands that I observed, for they might quite well be deformation bands or kinks.

As deformation is not homogeneous in the individual grains in a metal, there is no reason for the polygonization to lead to sub-grains which are all of the same size; and as a matter of fact, Figs. 7x (Plate XCVI) and 8x (Plate XCVII) of the paper prove that there is a mixture of sub-grains of different sizes, but they do not prove at all that these sub-grains are of a different nature. It is only because the polygonization may be more advanced in some more deformed parts that some areas will have small sub-grains and others coarse sub-grains.

The theory of dislocations also explains why the sub-grains are much larger in metal deformed by creep at high temperatures than in a metal which is annealed at the same temperature after being deformed at room temperature. In the latter case, where the metal is cold worked and afterwards annealed, the number of dislocations present in the metal is much higher, so that their re-arrangement into walls must lead to smaller sub-grains. This explains the very important fact referred to by the present authors, that recovery during creep is different from recovery after cold working. It is just a question of scale.

It may be concluded that the theory of dislocations, instead of hiding the concept of the sub-structure, explains it rather well qualitatively, and we hope in the near future to be able to publish some results giving a better quantitative explanation.

I should like to make one remark about the paper by Wood and Rachinger. The authors state that in a solid specimen the fact that the grains giving rise to back reflections have all the same orientation leads to the conclusion that they are strained in the same way. In other words, by this technique of a back-reflection ring on a solid specimen they conclude that they have eliminated the strain effects. I am not quite sure that this statement is correct, because if a grain has a (310) plane nearly perpendicular to the X-ray beam there is still a degree of freedom of rotation around the normal, and in addition the surrounding grains may differ in orientation, and this will lead to quite different internal strains. As a matter of fact, we have some experimental evidence for this.

MR. W. H. HALL,* M.A. (Student Member): By a careful choice of experimental conditions Dr. Wood and Mr. Rachinger have been able to differentiate between stress and particle-size broadening after cold working a number of metals. I wish to show that, in fact, the results of line-broadening measurements on randomly-oriented filings also confirm their results.

The suggestion that line breadths could be interpreted quantitatively on such a basis was first put forward by Dehlinger and Kochendörfer,† who applied it to measurements on rolled copper sheet and later to iron powders. The hypothesis has received mathematical support from Bragg,‡ who showed that at high diffraction angles such as those used by the authors the line-broadening due to the particle-size effect would be less than that due to internal stresses.

This argument can be extended in the following manner. In the limiting case of pure particle-size broadening the line breadth β_p is related to the effective particle size ϵ , the X-ray wave-length λ , and the Bragg angle θ by the equation: §

$$\beta_p = \frac{\lambda}{\epsilon \cos \theta}.$$

For pure strain broadening the breadth β_s is related to the effective strain η and the Bragg angle by the equation: ||

$$\beta_s = \eta \tan \theta.$$

If both types of broadening are present, the resultant line breadth β should be obtained by folding the component lines as described by F. W. Jones,§ Shull,¶ and Stokes,** but Wood and Rachinger have shown that for a commonly occurring line shape the breadths are additive, i.e.:

$$\beta = \beta_p + \beta_s$$

This assumption immediately leads to the following equation:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{\epsilon} + \frac{\eta \sin \theta}{\lambda}$$

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† *Z. Metallkunde*, 1939, 31, 231; *Z. Krist.*, 1939, 101, 134; *ibid.*, 1944, 105, 393.

‡ *Nature*, 1942, 149, 511; *Proc. Camb. Phil. Soc.*, 1949, 45, 125.

§ *Proc. Roy. Soc.*, 1938, [A], 166, 16.

|| A. R. Stokes and A. J. C. Wilson, *Proc. Phys. Soc.*, 1944, 56, 174.

¶ *Phys. Rev.*, 1946, [ii], 70, 679.

** *Proc. Phys. Soc.*, 1948, 61, 382.

If the line shapes are such that simple addition of the breadths is incorrect, a non-linear equation is obtained. For example, the assumption of Gaussian shapes leads to a hyperbola, shown dotted in Fig. A. In practice, the curve usually lies between these two extremes,* but the curvature at low values of $(\sin \theta)/\lambda$ is not easy to observe, since metals rarely diffract at such low angles, and for such lines the total broadening is small and difficult to measure. If, then, a straight line is fitted to the upper portion of such curves, the intercept $1/\varepsilon$ obtained will be too low, indicating an upper limit to the effective particle

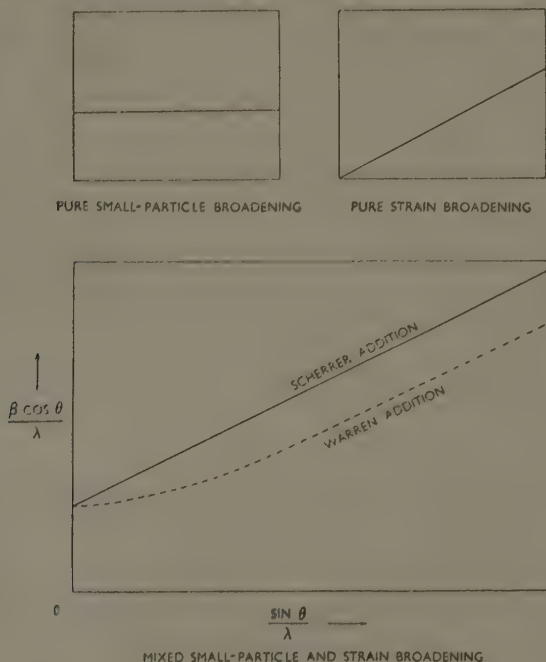


FIG. A.

size. In a distorted lattice the effective particle size ε must be interpreted as a measure of the volume of regions in the lattice which diffract coherently. In anisotropic metals the strain distribution is not the same for different crystallographic planes, and a relationship of the type:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{\varepsilon} + \frac{2\sigma}{E_{hkl}} \cdot \frac{\sin \theta}{\lambda}$$

is frequently a better representation of the experimental breadths. In this equation E_{hkl} is the value of Young's modulus for the direction perpendicular

* Jones (*loc. cit.*).

to the planes $\{hkl\}$ and σ is the Laue breadth of the stress-distribution function, which is assumed to be independent of direction.

I have analysed a number of published results by this method, and the best straight lines, determined by the method of least squares, are shown in Fig. B. Owing to the comparatively low accuracy of line-breadth measurements, the fit to these lines was not usually very good, but the general agreement between separate and independent sets of observations allows some confidence to be placed in the results. Since Wood and Rachinger measured only breadths at high Bragg angles, their results cannot be analysed in the same manner. However, it was pointed out to me by Mr. G. K. Williamson (Department of Metallurgy, University of Birmingham) that Table I of their paper shows that for iron filings, of a total breadth of 5.38 mm., 2.46 mm. could be attributed to particle-size effects and the remainder to variations of strain with direction in the randomly-orientated filings. These figures correspond to values of $\epsilon = 4.5 \times 10^{-6}$ cm. and $\eta = 0.48\%$, the corresponding line being shown dotted in the figure.

It will be seen that the slopes of these lines (i.e. the stress effects) increase progressively from soft to hard metals. The intercepts are all positive with the exception of that for martensite, and a comparatively small curvature of the line or error in the steep slope of the graph would account for this physically unreal result. In fact, Mazur* has recently reported results for which the intercept was positive. The mean value of all intercepts corresponds to $\epsilon = 10^{-6}$ cm. Owing to the uncertainty of the analysis, no more than the order of magnitude of this quantity, which is about the same as that determined by Wood and Rachinger, can be regarded as significant.

The physical significance of this value may be understood from the theory of dislocations. There is abundant evidence† suggesting that the maximum density of dislocations in most heavily cold-worked metals corresponds to an average distance between dislocation lines of about 10^{-6} cm. Since the dislocation lines are thought to be long compared with their separation, the coherently diffracting regions situated between neighbouring dislocations ought to have an effective particle size rather greater than 10^{-6} cm., which agrees well with the experimental values. Although recent calculations by Wilson‡ have shown that the approach described here is over-simplified, it seems fair to conclude that a much clearer understanding of the problem should result from direct calculation of line-broadening based on the dislocation model.

DR. N. P. ALLEN, § M.Sc. (Member of Council): I particularly welcome the paper by Wilms and Wood because it is a development of work which Dr. Wood started at the National Physical Laboratory, at the end of the war. It was then decided that it would be worth while to study creep by X-ray methods, which did not then appear to have been done. The work was begun with some trepidation, because we were aware that creep deformations were in general very small, and we felt that we might not get any results at all; but we were rewarded for our rashness by finding immediately that there was a very great difference between the amount of crystal breakdown caused by a certain amount of deformation carried out quickly and that due to the same amount of

* *Nature*, 1949, **164**, 358.

† G. I. Taylor, *Proc. Roy. Soc.*, 1934, [A], **145**, 362.

W. F. Brown, Jr., *Phys. Rev.*, 1941, [II], **60**, 139.

J. S. Koshler, *ibid.*, 397.

A. H. Cottrell and A. T. Churchman, *J. Iron Steel Inst.*, 1949, **162**, 271.

‡ A. J. C. Wilson, *Acta Cryst.*, 1949, **2**, 229.

§ Superintendent, Metallurgy Division, National Physical Laboratory, Teddington, Middlesex.

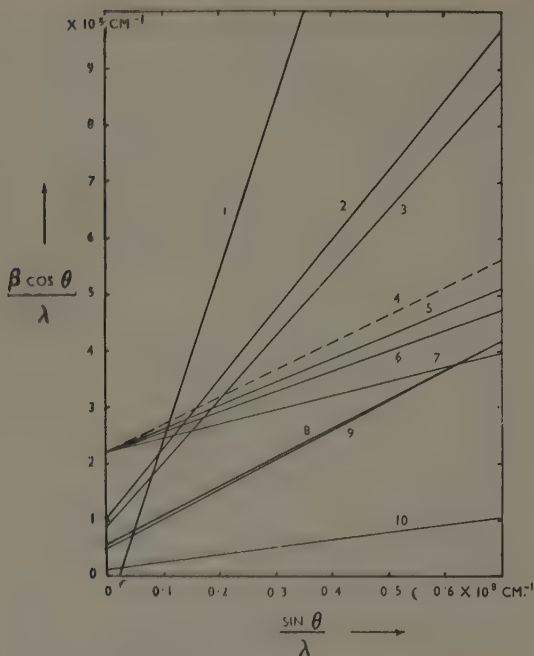


FIG. B.

KEY.

Line	Material	Radiation	Reference
1	Martensite rod	Iron	a
2	Rhodium filings	Zinc	b
3	" "	Copper	b
4	Iron filings	Cobalt	c
5	Copper sheet, rolled 99%	Copper	d
6	" " " 86%	"	d
7	" " " 20%	"	d
8	Copper filings	"	e
9	" "	Zinc	f
10	Aluminium filings	Copper	g

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- a. J. A. Wheeler and M. A. Jaawon, *J. Iron Steel Inst.*, 1947, **157**, 161.
 b. G. W. Brindley and P. Ridley, *Proc. Phys. Soc.*, 1938, **50**, 561.
 c. W. A. Wood and W. A. Ruchinger, *J. Inst. Metals*, 1949, **75**, 571.
 d. A. Kochendörfer, *Z. Krist.*, 1944, **105**, 898.
 e. A. R. Stokes, K. J. Pascoe, and H. Lipson, *Nature*, 1943, **151**, 137.
 f. G. W. Brindley and P. Ridley, *Proc. Phys. Soc.*, 1939, **51**, 432.
 g. W. H. Hull and G. K. Williamson, unpublished work.

deformation carried out slowly. The observation was described in a letter to *Nature* in the names of Wood and Tapsell.* It was also found at that time that a slow deformation at a given temperature did not produce the same effect as a quick deformation at that temperature, followed by annealing at the same temperature. It is important to realize that slow deformation is characteristically more gentle in its action, and does not disrupt the structure so much as fast deformation does.

At that stage Dr. Wood went to Australia and proceeded to examine the effect of temperature and rate of deformation on the phenomena, while the National Physical Laboratory continued the work on somewhat different lines. We prepared some rather coarse-grained specimens and examined the behaviour of the individual crystals by a Laue reflection method.

We were able to develop a technique whereby the centre of the crystal and the region near the grain boundary could be investigated separately, and to compare the behaviour of adjacent grains in the same aggregate. The results add something useful to what the authors have published. We confirmed that under slow deformations the amount of breakdown is extraordinarily small. After 5 or 10% extension the Laue spots are still quite clearly visible. It is possible to observe the relative motion of the adjacent grains, which does not amount to more than a few degrees, but is of the kind that one would expect from the ordinary theories of slip.

The interesting fact, however, is that the relative motion is not the same in all parts of the grain. Before deformation, a particular Laue reflection will be sharp. After deformation, the reflection from the centre of the grain will be displaced slightly, but will also have altered in form, and may be divided into two sub-spots. The reflection from another part of the same grain will have undergone similar changes, but not precisely the same changes; the reflection spot will have moved in a slightly different direction and broken down into a different number of sub-spots. The different parts of the grain are behaving in different ways.

In the early stages of deformation the spots are diffuse. After a while, the diffuse spots clarify themselves and become a number of sharply defined spots. One may imagine that the grain in the first place is divided into a number of areas which are distorted and have varying orientations, and that after a while these become little areas of uniform but slightly different orientation. It is interesting to note that that sub-division of the grains can be observed very clearly if the grains are subjected to anodic oxidation and examined under polarized light.

A further observation is that different grains and different parts of the grains are at different stages of these processes at the same time. I believe that is the reason why in the present paper it is recorded that spot reflections and diffuse rings may co-exist.

The authors consider that the slip leading to crystallite formation and the formation of "cells" are two different processes, but I believe that it is possible to think of the sub-division into cells as a natural consequence of the normal mode of deformation of a grain. Sir Geoffrey Taylor showed some years ago that in aluminium, in order to follow the external deformation of the specimen, it would be necessary for each grain to undergo slip in five different directions, and he was able to work out according to the orientation of the grain in relation to the direction of stress what the five orientations would be, how much slip would occur in each direction, and what the consequent rotation of the grain would be.

We normally think of the stress as uniform throughout the specimen, but in point of fact, because the grains are differently oriented, the stress

* *Nature*, 1946, 158, 415.

distribution in the metal is irregular. For example, if we have two grains and one is oriented in such a way that it does not easily slip, whereas the other is oriented in such a way that it slips easily, we find that the stresses tend to concentrate in the apparently hard crystal and to avoid the crystal which is apparently soft, and that continuous change of the direction of stress throughout the crystal occurs everywhere in the polycrystalline mass. The direction of stress in one part of the crystal is different from the direction of stress in another part, so that there will be a natural tendency for the movements of the one part to be different from the movements of the other part. That will show itself in diffuse reflections in the early stage of the experiment; but after a while some recovery will take place whereby each part will acquire a different but uniform orientation, so that we shall have slightly different orientations established in two parts of the same grain. I think it is very likely that some such mechanism as this is the origin of the breakdown into cells which is observed.

DR. W. HUME-ROTHERY,* F.R.S. (Member): I think that everybody will agree that these two papers are of extreme interest, but, as time is short, you will perhaps excuse me if I refer only to the points where we disagree rather than to those on which we agree. It is perhaps unfortunate that the authors have not made sufficient reference to the earlier work on the subject. The general idea of the splitting up of the crystal grain into sub-grains is quite old, going back at least to 1931 or 1932, and there has been extensive work since then.

I think that in their description of the alternative theories the authors have accidentally misrepresented the slip theories and the dislocation theories. In the paper by Wood and Raelinger, it is stated on p. 590 that the earlier theories gave no explanation of the hardening of a crystal during plastic deformation, but there is extensive work on this subject by Sir Geoffrey Taylor, whose dislocation hypotheses were extended to account for the hardening process.

I think that in general when one considers the work which Dr. Wood has done one wants to ask first whether the X-ray methods are satisfactory. I believe it will be found that a good many people are very doubtful of the value of back-reflection X-ray technique. By that method the X-rays are directed at the object and the reflections which come back at high angles are recorded. That means two things. In the first place, as in all reflection methods, it means that you tend to obtain predominantly what is happening at the surface of the metal, as distinct from what is happening inside. How far there is penetration into the metal will vary with the particular metal and the X-rays used. With aluminium the position will be more favourable than with lead, but with all X-ray reflection methods I feel that one tends to see more of the surface of the metal than of the interior.

Secondly, in back-reflection technique where only the high-angle reflections are obtained, all the information from the low-angle reflections is lost. In work which we have done at Oxford in other connections we have gradually been forced to the conclusion that arguments from the back-reflection method alone are often very dangerous. I think that that tends to go through the whole of Dr. Wood's arguments and his interpretations of his results. For example, he argues that because he gets the particular reflections which are on the circle and have moved a small way, therefore the crystallites have only very slightly different orientations; but he seems to forget that there may be other crystallites with widely variable orientations whose reflections have simply dropped out altogether because the X-ray technique adopted does not reveal them. I very much doubt whether it can be shown thoroughly what happens

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with a metal in the process of deformation unless a transmission photograph is used, in which the X-rays go through the crystal and therefore show more of the inside, and the arrangements are such as to reveal the whole of the X-ray reflections.

The second point to which attention should be drawn is whether the authors are justified in stating as dogmatically as they do that their temperature range is below that at which recrystallization occurs. In the first paper, they show a single crystal in which, in the original state, the orientation is such that you get the two dots for the one orientation, and then, after the deformation, they show the circle which is a completely resolved doublet. If you look at the photograph more carefully, you will find that not merely does it show the one completely resolved doublet, but part of a second doublet, and the doublets are all reasonably sharply resolved.

I have to speak without being able to find the particular reference, but I remember reading in the early days of deformation work that when you deformed crystals of aluminium at room temperature you obtained that kind of effect in which the doublets were resolved, but if you went down to a low temperature you then got fuzzy lines the whole way round. The interpretation given was that recrystallization had occurred during the deformation process. If you are not going to call it recrystallization, I think that you must define exactly what you mean by "recrystallization" much more carefully. After all, you have started with your one crystal, which has been so perfectly oriented that it has given two spots only, and after deformation you have a very different state of affairs; and if that is not recrystallization you must define what you mean by "recrystallization" very carefully.

It seems to me that the authors are simply making a new definition of recrystallization and implying that by recrystallization they mean not merely the forming of new crystals but that the new crystals have to expand so that the old crystal boundaries vanish as well. On the whole, I agree with what I understand was said by Dr. Sully earlier, that there is probably a general transition through the whole process. The crystallite formation at room temperature shown by the authors' first photograph is the first sign of a recrystallization, and from that you get larger cells inside grains, and then follows recrystallization with the expansion of the grains. I do not think that the authors should state so dogmatically that their work is carried out below the recrystallization temperature, particularly in the paper by Wilms and Wood, where they go up to temperatures of 250° and 350° C., because there I am quite sure that recrystallization is occurring, if one uses the word in some senses at any rate.

In the second paper the authors establish very clearly that there are two distinct types of deformation of the crystals, the one by slip, and the other at higher temperatures, where there is more movement of the grain boundaries; but I do not think that they have established anywhere in the paper that there is the kind of movement of the cells within the crystal which they claim. The photomicrographs seem to show clearly that there has been a very great upheaval of the grain boundary, and if there has been such an upheaval it seems to me that one can quite well imagine the deformation to occur in other ways. If there has been a tremendous disturbance of the grain boundary you can imagine the grains wandering a little and the grain-boundary material being responsible for it all, or there may be very fine slip going on all the time, and the temperature of 250°-350° C. is so high that the slip heals up continuously as it is going on, and you do not see the pronounced bands which you see in the ordinary low-temperature work.

I suggest in general, therefore, that the authors' experiments are of very great value, but that the interpretations which they place on them require thinking about more carefully, and that in a great many cases they have jumped

to conclusions. I should not myself accept their statement that their photomicrographs can be interpreted unambiguously. One may grant that their interpretation is the most probable interpretation of the results, but their experimental methods are not such that it is possible to give an unambiguous interpretation. They show only such a little of the whole truth that I do not think one can argue conclusively from them.

As Professor Greenwood is here, perhaps one may ask about one other point in connection with Dr. Wood's work which I think has not been appreciated by other workers. I have asked a large number of people this question, and have never been able to obtain a satisfactory answer. Dr. Wood claims that when you deform metals you obtain little crystallites, and you can set a maximum and minimum size to those crystallites. His claim that there is a minimum size is established; if there were no minimum size, the X-ray lines would go on getting broader and broader. A great many people, however, are much more doubtful whether there is any real validity for the claim that there is an upper limit of crystallite size, and it would be very helpful if the evidence for that could be set out much more clearly and satisfactorily. I have never seen it set out in full. Dr. Wood says that claims for upper and lower crystallite size are confirmed by experiments on sieved particles, but it is not possible to argue like that. If you agree that there is going to be more sub-division than you can see microscopically, then presumably, in sieved particles, the individual particles may contain smaller cells. It would be very helpful to everybody if the arguments in favour of the upper limit could be set out.

Mr. J. B. WILSON,* B.Eng., A.I.M. (Member): I think that the title of the first of these papers, "Mechanism of Creep in Metals", is probably its greatest defect. In fact it presents but one particular facet of the number of complicated mechanisms which go to produce what we know as creep, and it neglects to much too great an extent the contribution made by viscous effects in the grain boundary. Dr. Sully, when opening the discussion, answered quite a number of my questions on the respective parts played by the grain and by the boundary during deformation in creep. This paper, I think, tells us what can happen in the grain during creep deformation at a particular creep rate and in a particular range of temperature, but it does not offer any explanation why the amount of deformation in creep which can occur before rupture becomes less as the rate of deformation decreases.

It would seem to me that the mechanism proposed by the authors would allow for at least as much deformation at low rates of creep as is obtained at the same temperature and at higher rates. Thus I cannot see in the theory any explanation of the reduction, with decreasing stress, of the possibilities of deformation permissible before the first signs of rupture appear.

It is possible that the authors have not studied deformation at sufficiently low rates. Rates of the order of 10^{-5} or 10^{-4} cm./cm./hr. may be too high to show clearly effects corresponding to those which are so distressing when engineering materials are stressed under conditions where creep failure may occur.

The demonstration by Dr. Sully some months ago of tertiary creep in compression introduces another complication. It now seems to be fairly clear that tertiary creep can occur without an increase in stress resulting from reduction of gross area of cross-section or reduction of net area owing to the appearance of internal ruptures. It would be of interest to know whether the theory put forward by the authors can be applied to explain why tertiary compressive creep should occur.

My next point may not, I think, be entirely relevant, since the authors have

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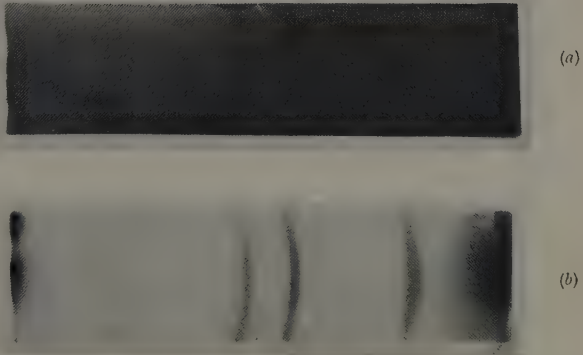


FIG. C.—Back-Reflection Diagrams of Cold-Rolled Brass (copper radiation),
(a) using unfiltered radiation,
(b) using $K\alpha$ doublet from a bent lithium fluoride monochromatizing crystal.

confined their studies to a pure metal in a very carefully controlled condition. The effect which I wish to mention is that of a precipitate in a binary age-hardening system. It is my observation—and it is borne out by work on the magnesium-cerium alloys by Mellor and Ridley *—that creep can be resisted in the presence of a precipitate. I have found that the maximum resistance to creep is brought about when the size of the precipitate is sub-microscopic. This would seem to indicate that even at low rates of deformation, say of the order 10^{-7} – 10^{-8} cm./cm./hr., movement is occurring which must be on planes of extremely small separation. I cannot see that such sub-microscopic precipitates would be able to block creep caused by the relative movement of sub-crystallites of the dimensions mentioned by the authors.

The majority of my criticisms of the paper are disarmed by its two final paragraphs, in which the authors make it clear that owing to the complicated nature of the creep process, they can only begin to examine it by defining their conditions of test extremely closely. I shall look forward to further contributions by the authors, in which they propose to consider other factors.

PROFESSOR GREENWOOD (*in reply*): There are one or two general matters to which I should like to refer, but I do not feel that I should attempt to reply in detail to this discussion, as the authors should have that privilege.

It has been mentioned that Dr. Wood has not given sufficient credit to previous workers. He has, however, related the phenomenon which he has described—namely, the fragmentation of crystals under prolonged stress—to the work which was done by Hanson up to 1939, and which was so aptly described in his lecture to the American Institution of Mining and Metallurgical Engineers.† In this he referred to what he then called “slipless flow”.

I think that the work of Wood and Wilms has clarified the characteristics of this slipless flow. In choosing a material such as high-purity aluminium for this work, we were guided by the properties of that material, namely the fact that it could be deformed readily at various temperatures and the fact that although it oxidizes it gives a transparent film, and so on. Also, it seems very clearly to demonstrate this cell formation, as other workers have so beautifully shown.

The general feature to which I would draw attention is in connection with an historical matter. I should like to recall to you that the early work on the deformation of metals and the demonstration of deformation by the process of slip was carried out by Dr. Rosenhain some fifty years ago. We feel in Melbourne that in some respects the work we are doing is a memorial to Rosenhain, because he was a Melbourne graduate who came to Cambridge in 1897 with an 1851 Exhibition. We like to feel that we are now carrying a stage further the work in which Rosenhain so early showed an interest.

With regard to the paper on creep, I look on it as a valuable contribution to a study of the mechanism of the deformation of metals. This deformation is referred to in the paper as “creep”, and, if one is satisfied with the definition of creep as “continuous deformation of a metal under stress”, then, of course, the phenomenon covered by the authors is creep. You will see that I am going to draw attention to a point mentioned by Mr. Wilson, that there are different types of creep.

To my mind, the term “creep” should be restricted to slow deformation over a prolonged period. Obviously the terms “slow” and “prolonged” are themselves sufficiently elastic to cover all that has been done on this subject. You will recall that many physicists have worked on creep and, perhaps in their anxiety to get results, have carried out experiments lasting half an hour.

* *J. Inst. Metals*, this vol., 679.

† *Trans. Amer. Inst. Min. Met. Eng.*, 1939, 133, 15.

That may appear to be "prolonged" stress to some people, but, of course, it is not in any way prolonged stress to the power engineer, who does not want any detectable deformation even over a long period of years.

We should give some consideration to what we really mean by "creep". In a recent paper (June 1949) which I presented to the American Society for Testing Materials, I suggested that to disentangle our thinking on the whole subject of creep we should acknowledge at least two different phenomena. If it were not that one of the terms has already been used to describe something else, I would suggest that we employ the terms "micro-creep" and "macro-creep". You will remember, however, that the term "micro-creep" has already been used by Chalmers to describe a certain phenomenon which he investigated. I would define "micro-creep" as that produced by low stresses and probably associated with crystal boundaries and minor lattice defects. I think that it is micro-creep in which the power engineer is really interested. The type of creep which has been described by Dr. Wood, on the other hand, I would refer to as "macro-creep".

How would we differentiate between these two? Macro-creep, I think, involves a deformation of the crystal as a whole, whereas micro-creep essentially involves either just the boundary material or the boundary material plus some minor portions of the lattice. In this connection I think the present paper is a valuable contribution, because it has shown us just the type of mechanism which causes macro-creep. I would point out that since these papers were published much more work has been done, and in particular in a third paper by Wood and Rachinger there is described a series of experiments which shows continuity of breakdown from ordinary temperatures to high temperatures, from rapid strain to slow strain. In general it can be said that the higher the temperature and the lower the rate of strain, the greater is the preponderance of slipless flow over slip. It is shown also that the size of the fragments or cells formed is greater the higher the temperature and the slower the rate of deformation, so that if you deform quickly at high temperature you tend to get fragmentation to smaller units than if you deform slowly at the higher temperature.

In connection with the difference between micro- and macro-creep, which I believe is important, there is a tendency to think that by operating under experimental conditions which give results quickly we are merely shortening the time of the experiment; but in my opinion under such conditions we are observing different phenomena, and therefore I feel that short-time creep tests which are being carried out in order to sort out materials are in effect useless and misleading. Short-time tests under conditions which give relatively rapid rates of strain are not dealing with what will ultimately be required in the engineering materials under low stresses giving low rates of strain.

On this note I would conclude. I feel that we should endeavour to define more closely the phenomena with which we are dealing. In that way we might avoid some of the confusion which unnecessarily arises when work of the kind which has been described by Dr. Wood as "creep" is related to the much lower rates of deformation which are characteristic of engineering conditions.

CORRESPONDENCE.

DR. W. BOAS* (Member): The interpretation of the well-known fact that broadening of X-ray interferences from metals is produced by cold work, has given rise to a long controversy, fragmentation and internal stresses being considered as the alternative causes. To decide between these views is difficult and is made more complicated by the fact that the results obtained by different workers using different X-ray techniques and methods of deformation cannot be compared directly. It actually seems that X-ray results alone will not be able to decide the question, and it is at least necessary to discuss the matter in conjunction with the effects of cold work on the shape of Laue spots and the intensity of interferences.†

With respect to filings, the cause of line-broadening is not in doubt and both sides agree that internal stresses are responsible for the effect. Whether one is allowed to apply the results obtained on filed powders to polycrystalline specimens has been disputed, as filing produces inhomogeneous strains. However, even in a tensile test which gives a macroscopically homogeneous deformation, the strain within each crystal is highly inhomogeneous on a microscopic scale, owing to the interaction of the crystals at their boundaries.‡ This is important in X-ray work, as the irradiated volume of the metal specimen is small but still large enough to contain strain gradients. Further, Bragg has recently advanced a theoretical argument that line-broadening due to strain swamps that due to small crystal size.§

The authors emphasize that the hardness of a cold-worked metal is related to the broadening of the X-ray rings. This seems to be the case in their experiments, but I think it would be dangerous to generalize their conclusion. Dehlinger || has shown that different types of deformation which produce the same increase in hardness, do not give rise to the same broadening. Crussard ¶ reports that a second deformation, in the reverse sense to the initial one, leads to a decrease in line width although the hardness increases. Further, the restoration of the line sharpness on annealing does not occur parallel with softening, in all metals.** The conclusions have therefore to be drawn that there is no simple general relationship between line-broadening and work-hardening, that the stresses produced by deformation make an important contribution to line-broadening, and that even in polycrystalline materials fragmentation (if it occurs), being irreversible, cannot be the major cause of line-broadening.

The boundaries of the fragments which are supposed to give small particle-size broadening, should not be confused with the type of boundary formed in a crystal in which a dislocation has ceased moving, thus causing a discontinuity of one atomic distance.

The authors object to a picture of flaws, as the strength of a metal would not be reproducible on this assumption. In this connection reference should be made to the proof of the statistical character of the brittle strength of solids such as glass and quartz.††

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† W. Boas, *Rev. Mét.*, 1949, **46**, 84.

‡ W. Boas, *Helv. Phys. Acta*, 1950, **23**, (1/2), 159.

§ W. L. Bragg, *Proc. Camb. Phil. Soc.*, 1949, **45**, 125.

|| U. Dehlinger, *Ann. Physik*, 1929, [v], **2**, 749.

¶ J. Crussard, *Phys. Soc. : Rep. Conf. on Strength of Solids*, 1948, 119.

** J. E. Wilson and L. Thomassen, *Trans. Amer. Soc. Metals*, 1934, **22**, 769.

F. Nieman and S. T. Stevenson, *Phys. Rev.*, 1942, [ii], **62**, 330.

†† A. Joffé, *Internat. Conf. Physics, London*, 1934, Vol. II, 77.

Finally, I wish to emphasize that the accuracy with which the line width is usually determined by the photographic method is not sufficient to draw firm conclusions. We are at present engaged in measuring intensities and line widths using monochromatized radiation and Geiger counters. In particular the use of strictly monochromatic radiation seems to be essential for this purpose, as shown in Fig. C (Plate CXXXI).

DR. F. ROHNER * (Member): This paper is of fundamental importance in the explanation of work-hardening. It shows conclusively that work-hardening is not the effect of internal strains, but that it is caused by crystallite disintegration.

Up to now internal strains and crystallite disintegration, which both accompany working, could not be separated, either by X-ray diffraction or by other means. Wood and Rachinger have succeeded in separating the two effects in two independent ways, and they have shown that work-hardening proceeds parallel with the crystallite disintegration and not with the internal strains. This means a severe shock to the orthodox view that hardening effects are quite generally caused by internal strains. In its application to age-hardening it means a new argument against theories which attribute the hardening to internal strains, caused by precipitates or pre-precipitates of any form.

The AUTHORS (*in reply*): In the first place, we would like to record our thanks to Professor J. N. Greenwood for kindly presenting the papers on our behalf. We were already in his debt for the active encouragement and discussions that lightened the work during its progress.

We were very interested in Dr. Sully's remarks. Perhaps his first point regarding the possible relation between the cell structure studied in our paper and the Lacombe-Beaujard structure is answered by the notes that were read at the beginning of the discussion. We may emphasize here, however, that our own concern is primarily with a sub-structure that is created by the action of deformation itself; one that varies systematically not only with the temperature but also with the rate of strain; and one that would be superposed on any preliminary structure that might be present in the specimens before deformation. Sub-structures in the metallic grain, however produced, are, of course, all part of one big subject. We feel, however, that some confusion will be avoided if, first, the sub-divisions in the field are clearly recognized; and in particular, if a distinction is made between the structures produced when deformation and heating are separate operations, as in recovery, and those discussed in the paper on creep where deformation and heating are concurrent. We have done sufficient further work to show that any apparent relation is superficial. An example is the comparison of size mentioned by Dr. Sully; for it has already been indicated that our cell size varies according to the conditions of deformation.

The further remarks by Dr. Sully on the viscous behaviour of the grain boundary and sub-boundaries at elevated temperatures are very much to the point. It is evidently one of the main factors in creep; so much so in fact that we wonder whether work on "boundary-less" single crystals, which he suggests, would really help in explaining the creep of polycrystalline metals.

Dr. Sully is quite right in suggesting that there need be no connection between the sub-structure and the elongation of specimens to fracture, and we should not wish that implication to be read into the sentence that he quotes from the paper. Our point was that in creep the shape of a grain in the polycrystalline aggregate, amongst other things, has to follow the

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general change in shape of the specimens. If the viscous grain boundary cannot produce this change of shape—and this is hardly likely, for instance, at lower temperatures—then the change of shape must involve internal breakdown of the grain; otherwise the boundaries would part.

Mr. Eborall's picture of the deformed state is very interesting, but we find it difficult to follow his argument. He admits that the broadening due to small particle size is present in the X-ray lines from cold-worked metals, but suggests that this cannot be taken as evidence for the presence of small particles or crystallites in the metal. It can hardly be taken as disproof! He would imply that there are small coherent units in the grain, but that it would be wrong to call these "crystallites" because they may be separated by a locally curved lattice, and not a sharply defined boundary. But on the atomic scale, except possibly between twins, there can be no such thing as a sharply defined boundary, and it is hardly necessary to labour the point that the units or crystallites must be separated by a zone of misfitting atoms. We do, however, suggest that it would be contrary to the experimental observations if it were assumed that this zone occupied an appreciable volume.

Mr. Eborall states that we have conceded the point that in most of the experiments by other workers line-broadening due to random stresses predominates. We feel that it would be truer to say that this point has never been in doubt. In quite early papers by Wood* the point was made that, in general, line-broadening due to internal stresses and that due to small crystallite size are present together. Thus we may quote the following sentence from the 1939 paper: "The metal accommodates itself to its external deformation by the dispersion into and relative movements of the crystallites, but this process is accompanied, in the general case, by the incidence of measurable internal stress in the lattice."

Mr. Eborall raises the important point, how fine crystallites in cold-worked metal could be related to the large blocks revealed in a grain by heating a lightly worked metal during recovery. This deserves a fuller answer than we can give here. But, very broadly, in such metal we should consider the blocks to be already formed by deformation. We should identify the blocks with the regions between the slip lines; and the crystallites with a fine structure between the blocks. The crystallites would be a kind of debris of transitional orientations, corresponding, if it could be seen, to a fine structure of the slip lines. In slipless creep, we consider the amount of debris to be negligible. In heavy cold deformation, the blocks will be progressively reduced.

Mr. Eborall then suggests that it is necessary to assume a curved lattice, which, on heating, forms the blocks by local straightening (polygonization). On the contrary, there is a simpler explanation which we much prefer to the concept of polygonization. In our view recovery consists merely of the progressive absorption of the finer crystallites into the larger blocks already formed. We find that this explains the changes in the X-ray photographs quite effectively. It follows, of course, that it should be possible with sufficient resolution to observe signs of the blocks in the X-ray photograph of the metal before heating. We note that Mr. Eborall in his own experiments has not been able to find any signs. That, however, is not our own experience, and we are interested to note that neither is it the experience of Professor Crussard, as he mentioned later in the discussion.

We welcome the account given by Professor Crussard of his further work, in which we are extremely interested. In general his observations agree

* W. A. Wood, *Trans. Faraday Soc.*, 1935, 31, 1248; *Proc. Roy. Soc.*, 1939, [A], 172, 240.

with our own. We should like, however, to reserve judgment on his theoretical interpretation, and in particular on his suggestion that our observations on the cells are explicable by polygonization. There are many objections. Thus the concept of polygonization involves a two-stage process. First, a distortion or disorientation of the structure that gives rise to diffuse X-ray arcs and, second, a fragmentation of the disoriented structure which transforms the arcs into separate sharp spots. But we find that in creep it is quite easy to produce the sharp spots at once, without any prior disoriented state. It might be said, of course, that the first state of polygonization is over in an infinitesimally small time. But this is the same as saying that it need not take place at all. The general relation between the size of the coarser sub-structures formed in deformation and the spacing of the slip lines, observed by Professor Crussard and ourselves, is, we feel, highly significant. It has suggested to us the alternative to the idea of polygonization already mentioned.

Professor Crussard's final point about measurement of the X-ray reflection rings is theoretically correct, but in practice of no significance. The strain at right angles to the specimen corresponds to a minor axis of the strain ellipsoid. About that axis the variation in strain is a minimum and is in practice within the limits of experimental measurement. In any case the effect can be allowed for by confining measurement to the same radial direction in the different diffraction rings.

We should like to congratulate Mr. Hall on the neat and elegant extension of the observations in our paper. It will be possible as a result of his method to separate the line-broadening due to internal stress from that due to small particle size in the more complicated cases. In this paper we were concerned with determining the contribution due to the small crystallite size. We feel that in such a case it is perhaps better that the larger contribution due to internal strains should, as far as possible, be eliminated experimentally, since it is in the nature of a correction. This does not detract, however, from the great value of Mr. Hall's contribution.

We were very interested to learn from Dr. Allen's remarks that the particular work on creep initiated at the National Physical Laboratory by Wood and Tapsell has been continued. The results that Dr. Allen describes are highly significant in showing the relative movement of various parts of the grain. We should agree in general with his explanation of the formation of sub-structures as the result of differential deformation within the metallic grain. The only point is, that we are not certain that the simple Taylor hypothesis is entirely sufficient, because there is considerable evidence to show that the deformation of a single crystal in the polycrystalline aggregate is more drastic than would be indicated by the theories put forward by Taylor.

We are not unaware, as Dr. Hume-Rothery would imply, that the splitting of grains into sub-grains has been discussed for many years. But we are certain that the recent X-ray and metallographic observations now accumulating in various laboratories, despite his misgivings on the technicalities involved, are creating quite a different picture of recovery and deformation from that which has been available hitherto. With regard to the queries on technique, it is well known that the usual X-ray methods concentrate on the surface of a metal; but that surface can be dissolved away. The microscope is an even greater offender in that respect; but no one would wish to discard it. We have used the transmission techniques and small-angle reflections mentioned by Dr. Hume-Rothery. Our experience showed that as far as the new effects were concerned, there was nothing at all observable by these methods that was not shown up to much better advantage by the back-reflection method.

With regard to recrystallization, it is well known that the effect depends on the degree of deformation, time of heating, and temperature. The term normally has quite a simple direct meaning; and it is not difficult to carry out tests to find whether recrystallization has or has not occurred. In the recognized sense of the term, we can state that the conditions of deformation were such that no recrystallization occurred during deformation in our specimens.

In reply to his final query, our point is that extensive cold working must reduce the grains to fragments of the size required to produce continuous X-ray rings from a stationary specimen. If we take metal filings and photograph the coarser particles, the X-ray ring will consist of separate spots. By taking smaller and smaller sizes of particles, the spots are multiplied until the ring appears continuous. This stage is a rough guide to the upper size in question.

We agree with Mr. Wilson that a considerable range of strain rates must be examined before a final picture of creep is obtained. Further, by the nature of the subject, this will take many years. But that is no reason why a beginning should not be made, and it is, of course, tempting to begin with the higher rates of strain. This point, however, is dealt with more fully by Professor Greenwood.

We feel that Dr. Boas, in his remarks, is raising a wrong issue. It is not nowadays a question as to whether fragmentation or internal stress should be the cause of X-ray line-broadening. This is clear from the contribution, for instance, by Mr. Hall. The problem now is to determine the contribution from the separate effects; for in a cold-worked metal both effects will in general be present. Lack of appreciation of this point is probably the reason for Dr. Boas's confusion as to whether the hardness of a cold-worked metal is or is not related to the broadening of the X-ray rings, for few workers have made it clear whether the broadening to which they refer is that due to internal strains or that due to small particle size or a mixture of the two. With regard to the final point made by Dr. Boas, we do not feel certain that the use of "monochromatic" radiation will have the advantages in this problem that he claims. For the radiation in fact is not monochromatic, but a narrow band of radiations. At the high angles of diffraction which are necessary for sensitive measurements, this band will extend beyond the limits of the X-ray line being determined. Monochromatic radiation has its uses, especially in the detection of faint lines, but that is a different question from measuring the shape of an individual line.

We thank Dr. Rohner for his contribution and we are very interested in his suggestion that it might be possible to consider problems of precipitation-hardening from the view point of grain breakdown.

DISCUSSION ON PAPER BY MR. A. B. MIDDLETON, DR. L. B. PFEIL, AND DR. E. C. RHODES: "PURE PLATINUM, OF HIGH RECRYSTALLIZATION TEMPERATURE, PRODUCED BY POWDER METALLURGY."*

(*J. Inst. Metals*, this vol., p. 595.)

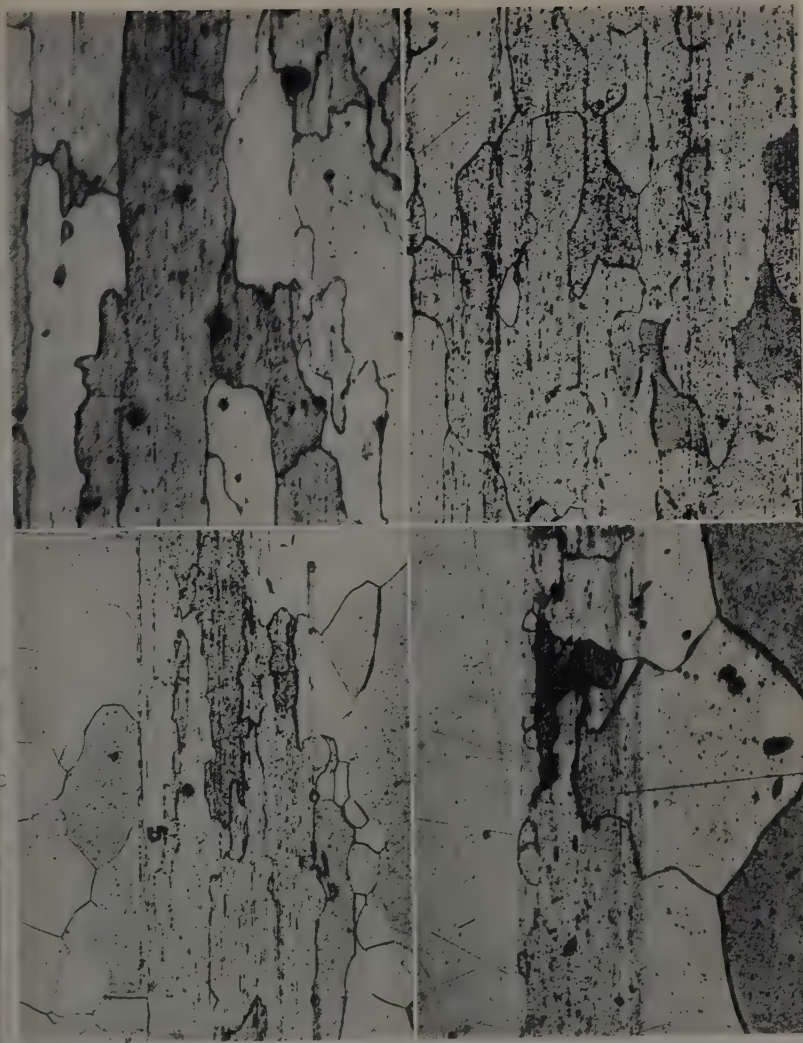
DR. J. C. CHASTON,† B.Sc., A.R.S.M., F.I.M. (Member): This paper is, I think, of wider interest than the title may suggest, and I believe that the greatest compliment to pay the authors is to ask them for more. Before discussing some of the further questions which arise, however, I think it may be useful to examine how far commercial platinum made by powder metallurgy exhibits a fibrous structure.

Fig. A (Plate CXXXII) may put the matter into perspective. This shows a structure which I think is typical of that found in commercial pressed platinum which has been cold drawn by 92%, before annealing for $\frac{1}{4}$ hr. at 1200° C. There is certainly evidence of a persistent elongated structure in the direction of rolling, but the metal is not nearly as fibrous as many of the laboratory samples shown by the authors, and in fact even in the laboratory we have never been able to get quite such persistent fibrous structures as are shown in the author's Fig. 4 (Plate LXX). The reason may lie in very slight differences in working technique. The authors appear to have carried out all initial working by swaging, but in our laboratory work we always hammer-forged the compacts immediately after pressing before proceeding in the manner described in the paper.

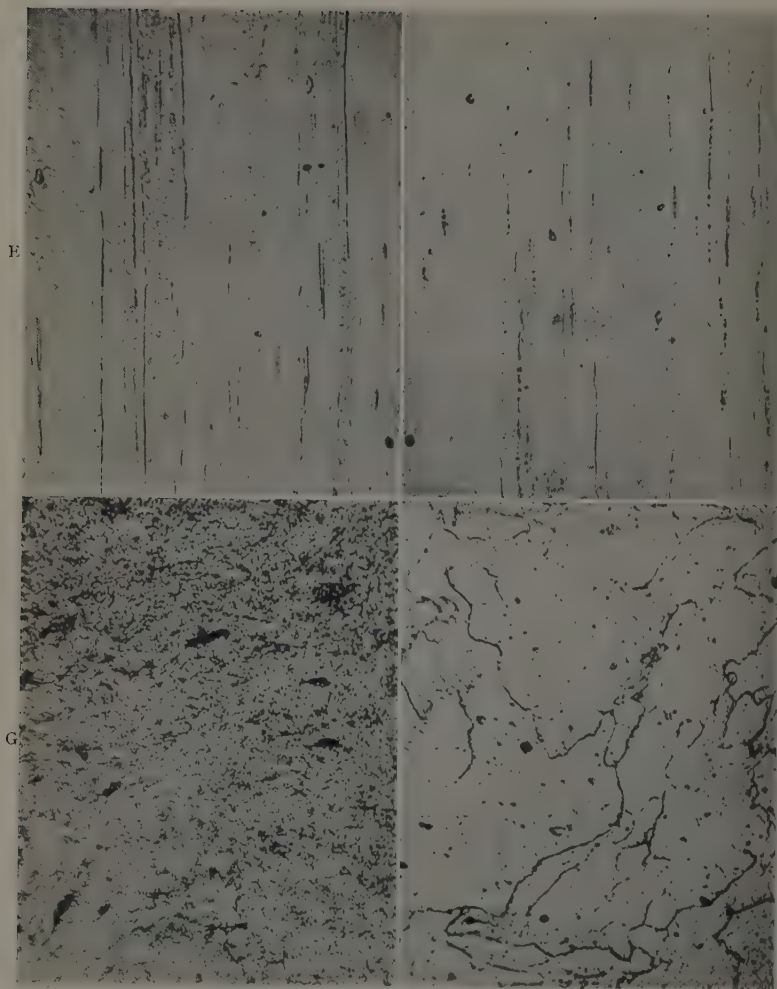
As to the cause of the persistent fibrous characteristics, the authors have made a very good case for the view that the differences between sintered and melted platinum are due, not to impurities, but to "suitably dispersed porosity". When I first read the paper, it seemed to me that there was one further impurity which might be considered, namely air, or rather the nitrogen in the air. If air were entrapped, it might play an important part in preventing consolidation. Oxygen might diffuse through platinum and escape, but the residual nitrogen would be expected to remain (perhaps as a film adsorbed on the surfaces of the particles) and hinder recrystallization and grain growth. We did one or two experiments to see whether there was any support for that view. A compact was made up from a mass of powder, loosely distributed in a platinum boat. The boat was placed in a tube and the pressure reduced to about 10^{-3} mm. before heating, after which the mass was sintered—still in vacuum—at 900° C. The structure of the wire produced from this compact (final cold reduction 92%) after annealing for $\frac{1}{4}$ hr. at 1200° C. is shown in Fig. B (Plate CXXXII). The structure, while not far from being equi-axed, shows some slight evidence of directionality; and the result, while, of course, not conclusive, suggests that entrapped air is not likely to be the only cause of this effect.

* Discussion at the Annual Autumn Meeting, Paris, 7 October 1949.

† Chief of Metallurgical Research, Johnson, Matthey and Co., Ltd., Wembley, Middlesex.



- FIG. A.—Commercial Pressed Platinum. Cold drawn 92% and annealed at 1200° C. for $\frac{1}{4}$ hr. $\times 80$.
- FIG. B.—Wire from Unpressed Powder, Sintered in Vacuum. Cold drawn 92% and annealed at 1200° C. for $\frac{1}{4}$ hr. $\times 100$.
- FIG. C.—Sheath-Rolled Platinum, with Tube Evacuated. Wire drawn 92% and annealed at 1200° C. for $\frac{1}{4}$ hr. $\times 80$.
- FIG. D.—Sheath-Rolled Platinum; Tube not evacuated. Wire drawn 92% and annealed at 1200° C. for $\frac{1}{4}$ hr. $\times 100$.



FIGS. E-H.—Longitudinal and Transverse Sections of Sintered Platinum Wires as drawn (Figs. E and G) and after heating at 600° C. for 15 min. (Figs. F and H). Electrolytically etched in NaCl-HCl solution using A.C. $\times 1000$.

FIG. E.—As drawn. Longitudinal section.
 FIG. F.—Heated at 600° C. Longitudinal section.
 FIG. G.—As drawn. Transverse section.
 FIG. H.—Heated at 600° C. Transverse section.

Some further light on the mechanism is, I think, shown by the results of two other experiments. We made two compacts by "sheath-rolling" in a platinum tube, one after evacuation of the tube, and the other with air present in the tube. The platinum powder was packed in a platinum tube which was sealed (in the one case after reducing the pressure to 10^{-3} mm.) and the tube then rolled, swaged, and drawn to a final dia. overall of 0.042 in. As will be seen from Figs. C and D (Plate CXXXII), the sheath-rolling treatment (which is known to be particularly effective in promoting intimate contact between the particles) has been successful in breaking down or eliminating all barriers to grain growth, and there is no trace of directionality—except in the centre of the wire—in either sample.

In considering the implications of this work, it appears that there are three factors which may influence directionality: the shape of the particle, the presence of entrapped air between the particles, and the presence of adsorbed gas on the surface of the particles. As to the first, the shape of the particles of powder made by decomposition of platinum salts is extremely irregular. Each particle is a jagged, spiky, and often porous structure—really unsuitable for any theoretical analysis. I have thought for a long time that precious-metal powders should be particularly suitable for experiments designed to study the theoretical bases of sintering, as they are not subject to complications through the formation of oxide films. But the authors' experiments emphasize that if they are to be used for this purpose they must be produced in regular shapes, and that the possible effects of films of adsorbed gas must still be taken into account.

In conclusion, it is obvious that a good deal more work needs to be done before the exact cause of these elongated structures can be established. I do not think that there is much doubt that the essential reason for this directionality is the inability of grain growth to jump across small gaps in the structure. I believe, however, that there must still be some uncertainty as to whether these gaps are simply cavities which are not closed up by the methods of working employed (although they can be closed up by more drastic methods of consolidation such as by sheath-rolling), or are filled with entrapped or adsorbed surface films of gas. The few experiments which we have done certainly suggest that the latter effect—that of entrapped gas—may not be all-important.

PROFESSOR DR.-ING. A. VON ZEERLEDER* (Honorary Corresponding Member to the Council for Switzerland): My collaborator, Dr. Rohner, and I have been very much interested in this paper. At Neuhausen we have done similar work with aluminium powder and got similar results, namely, a higher recrystallization temperature than with cast aluminium and higher tensile strength, both at ordinary and at elevated temperatures. We have described our results in a patent specification and in a paper to be published in a special volume of the proceedings of the Swiss Society for Testing Materials, which will be published in a few weeks.

Fig. J shows the process by which we are making the components of aluminium powder. We take powder with a specific gravity of 0.1, and this is first compressed cold in a normal atmosphere at 20–50 kg./mm.², and the great reduction in volume which occurs will be noted. It is then sintered at 500°–600° C., normally in the atmosphere but sometimes in hydrogen or another inert gas, and is hot pressed at 50 kg./mm.², so that the specific gravity becomes 2.7. These small billets are then put together to make a large billet for extrusion, and extruded to bars at 500°–600° C. and a pressure

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of 50–100 kg./mm.² That is higher than is needed with any aluminium alloy. It is surprising that pure aluminium demands such a high pressure at the very high temperature of extrusion. The specific gravity is then 2.8, which is about the same as normal extruded aluminium.

Fig. K shows the influence of the grain-size of the powders on the tensile strength and hardness of aluminium, and also the yield point of this aluminium in the extruded state. The grain-size of the different powders is shown, and it will be seen that with a finer powder there is an increase in the tensile, yield,

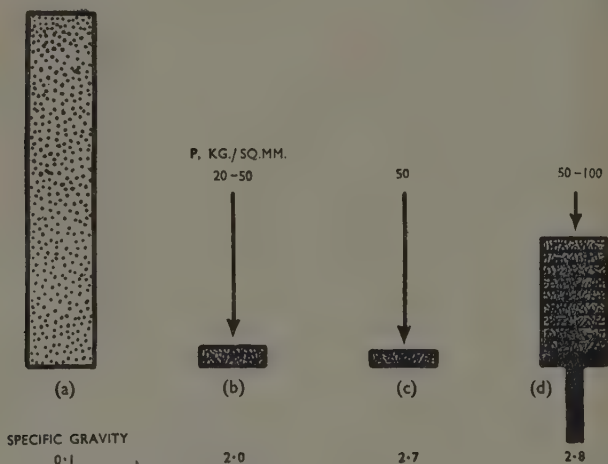


FIG. J.—Production of Sintered Aluminium Powder.

KEY.

- (a) Aluminium powder.
- (b) Cold pressed at 20–50 kg./mm.²
- (c) Sintered at 500°–600° C. and hot pressed at 50 kg./mm.²
- (d) Extruded at 500°–600° C. and 50–100 kg./mm.²

and hardness figures of the extruded pure aluminium. The tensile properties are much higher than those of cast and extruded pure aluminium. The elongation is given by the curve at the bottom.

Table A gives a comparison of the qualities of this Sintered Aluminium

TABLE A.—Properties of SAP Compared with those of Ordinary Aluminium.

	SAP	Al
0.2% proof stress, tons/in. ²	16–22	1.3–3.2
Ultimate tensile strength, tons/in. ²	19–26	4.5–6.5
Elongation, %	3–10	20–35
Brinell hardness, tons/in. ²	51–64	13–19
Electrical conductivity, m/Ωmm. ²	23–26	34–36
Thermal conductivity, cal./cm.sec.° C.	0.4	0.5
Thermal expansion, cm./cm. ° C. × 10 ⁻⁶	19–20	24

Powder, which we call "SAP", compared with pure aluminium. It will be seen that the proof stress, the ultimate tensile strength, and the Brinell hardness are much higher for the SAP material. This astonishing analogy between two metals otherwise so different from one another as platinum and aluminium may be taken as an indication that these special properties of sintered powder compacts cannot be fortuitous, but must be of a quite fundamental nature. It is to be expected that theoretical information of the greatest importance can be derived from them.

The present authors attribute the special properties of the sintered platinum compacts to "a small amount of suitably dispersed porosity". They suggest that this porosity has the effect of hindering recrystallization. We agree with

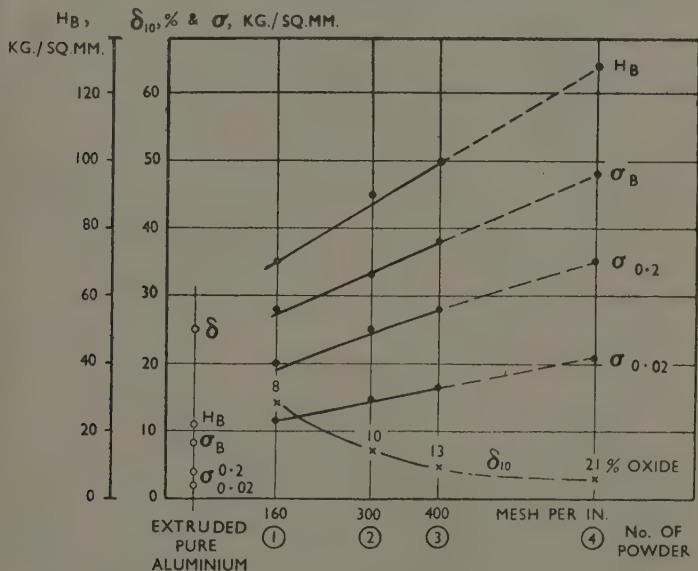


FIG. K.—Effect of Fineness of Powder on Strength.

them, but we are surprised that they refrain from discussing the effect of this porosity at ordinary temperatures. It seems that only the behaviour of their powder compacts at elevated temperature is of importance to them, and they almost ignore the fact that at ordinary temperatures they find a hardness number of 126 for wire produced by powder metallurgy, as against 94 for ordinary wire.

If we consider this increased hardness in relation to the "small amount of suitably dispersed porosity", a possible connection with the vacant-lattice-site theory of age-hardening is obvious. A suitably dispersed porosity has, in both cases, the effect of reducing the size of the crystal elements with an ideal lattice architecture. Each elementary slip process cannot extend beyond such a crystal element. As a result, the vacant lattice sites or the pores

reduce the free path of slip and therefore increase the hardness and strength of the metal.

There is a further connection with the crystallite theory of strength, developed by Bragg and by Wood. The powder particles continue to exist in the sintered compact as separate crystallites, for X-ray diffraction shows that there is no recrystallization and no grain growth in our sintered and extruded aluminium product, even after 500 hours' annealing at 500° C. Now, the size of the powder particles, and consequently of the crystallites of the powder compact, lies far below the limiting crystallite size obtained by the cold working of the cast metal. The size of the crystallites is 10 to 100 times smaller than the finest grain of a cast and extruded aluminium bar. The hardness and strength of the powder compacts must therefore be higher than those of cast metal cold worked to the maximum extent.

This point of view is not in conflict with that mentioned above, based on pores or vacant lattice sites. Grain and crystallite boundaries are, to a certain extent, constituted by vacant lattice sites, and so the vacant-lattice-site theory of age-hardening and the crystallite theory of strength of metals have a common basis.

I wish to put two questions to the authors. First, have they really found an increased hardness in their wires at room temperature? Is it correct that the platinum wire produced by powder metallurgy has given a hardness number of 126, as against 94 for wire produced from the same platinum by ordinary procedures? Secondly, do the authors think that it is worth while taking into consideration the crystallite theory of strength and the vacant-lattice-site theory to explain the increase of hardness and of tensile strength of their platinum wire compared with the cast platinum wire?

DR. A. G. DOWSON,* M.A., F.I.M. (Member): I agree with Dr. Chaston that this is a most important development, and one which requires a good deal of further elucidation.

It would, perhaps, be of interest to give a little more of the history of this development, i.e. the production by a powder process of platinum with properties superior to those of platinum produced by normal melting processes. I believe that it started in the requirement for improved sparking-plug electrodes for aircraft engines, because, before and during the early part of the war, the electrode was becoming the limiting factor in the performance of aircraft engines, the working temperature of which was increasing all the time.

One of the first things that was found to be important was this fibrous structure referred to by the authors, which is obtained by very large amounts of cold working. The Mond Nickel Company showed that wire with this structure had very much improved properties in resistance to lead attack; but, of course, at operating temperatures, it recrystallized. The next step was the suggestion of Dr. Smithells, following his work on tungsten, that this recrystallization might be retarded if there were put into the platinum or platinum alloy—it was platinum-tungsten with which we were concerned—some non-metallic constituent, which might interfere with grain growth and thus retain the desirable fibrous structure when the metal was heated to a high temperature in service.

My Company, in collaboration with Dr. Smithells, quickly did a great deal of work on this matter, and we found that by incorporating thorium by a powder technique, we got wires which were so good that no one questioned the explanation as to why they retained their fibrous structure. There is still some doubt whether this is the same thing as the possession of a high recrystallization temperature, and Dr. Smithells is not convinced that there is no

* Baker Platinum, Ltd., Slough, Bucks.

recrystallization. He suggests that it may be merely a question of the form in which recrystallization takes place. That, however, is not very important; a satisfactory structure and good mechanical properties are retained. Very large quantities of wire have been produced with the oxide addition, and the electrodes gave, and are still giving, excellent service.

I think it was about the time that large-scale production was getting under way that The Mond Nickel Company told us that they had found that, as reported in this paper, they could get an apparently similar result without putting in any non-metallic substance at all. We were very surprised at this, and our thoughts were on the same lines as those of Dr. Chaston. We thought that if we did not put anything in, there must nevertheless be something there to restrain grain growth. The authors have taken some pains to discount this idea, which evidently occurred to them also, but I think they are throwing hostages to fortune when they say in the discussion of their results, that "the suggested effect would probably be valid whether the pores were vacuous or filled with gas or with an inert solid phase". I find it very difficult to visualize a pore remaining as such after hot working followed by very severe cold working, and still more is it difficult to believe that a hole full of vacuum would prevent atoms of platinum which normally weld together very readily, from doing so. Dr. Chaston mentioned that platinum is entirely free from oxide films. That is certainly what I was brought up to believe, but I am now not quite sure that there is not a film of some kind. There are disturbing references in the literature (which I have been studying a good deal lately), and I would very much like to see the matter re-explored.

Another point made by Dr. Chaston was that he produced by sintering in vacuum some sheet which showed normal recrystallization on the outside. I do not know what size of sintered compact he started with, nor how it was worked, but if he reduced the cross-sectional area cold by 92% he must either have started with a very thick bar or have finished with a very thin sheet. This phenomenon, as the authors point out, is found in a far more marked way in wires than in sheet.

DR. CHASTON: The compact was drawn to wire of the same size as that of the authors. It was not flat rolled.

DR. DOWSON: I'm sorry, I thought Dr. Chaston said that it was flat rolled; but although it is not relevant to Dr. Chaston's remarks, the fact is of some importance. If you try to produce sheet you do not get the same enhanced properties nearly so readily. We have, however, had some promising preliminary results with sheet of oxide-bearing alloy used in apparatus for handling molten glass.

Dr. Chaston raised a number of other points which I would have liked to discuss, but in view of the shortage of time, I will leave them to the authors who are in any case better qualified to deal with them than I am; however, if as it seemed to me, the burden of Dr. Chaston's remarks is that he finds the phenomenon difficult to reproduce, I would say our experience is that by following exactly the authors' directions, we have got the reported results. I would agree that very careful control is required, and it is perhaps fortunate that the development of oxide-bearing materials came first, since the procedure for their manufacture is not quite so critical. Further, we have found that platinum and platinum alloys to which additions of oxide have purposely been made show higher strength at room temperature, and the property of resisting softening when heated to high temperatures very much more markedly than platinum as produced by the authors. But perhaps the most important difference is the fact that the manufacturing procedure is far less critical. If we take platinum which has had no oxide addition and compare it with

specimens containing progressively increasing amounts of thorium oxide, all sintered at the same temperature, we get a family of curves not dissimilar from those reported here for platinum sintered at different temperatures. If we sinter all our bars at 1400°C. , pure platinum, as shown in Fig. 13 of the paper, follows fairly closely the curve of regular platinum, while wires with increasing additions of oxide give curves similar to the ones shown for pure platinum sintered at lower temperatures.

We have, therefore, continued to put oxide into our platinum alloy for sparking-plug electrodes because we can get better properties, namely greater tensile strength and hardness, with a good deal more flexibility in the method of working. That was, of course, very important during the war, and it is still important when one is producing on a commercial scale. We are regularly sintering and working bars 8 in. long by 1 in. square, and getting very consistent results. I believe that to obtain comparable results without adding oxide, the procedure would be a good deal more critical.

CORRESPONDENCE.

MR. R. H. ATKINSON *: Whilst the authors have made a notable contribution to the powder metallurgy of platinum, I would like to point out that there may be an alternative interpretation of their results which they do not mention, namely, that the increased strength of their product at high temperatures is due to abnormal hindrances to grain growth rather than to a raising of the temperature of recrystallization. The very fineness of the fibrous structure makes it difficult to detect recrystallization micrographically in longitudinal sections until grain growth has proceeded far enough to develop relatively coarse columnar crystals. However, I have found that when transverse sections of sintered platinum wires are examined, there is a very noticeable difference in structure between as-drawn wires and wires that have been heated for 15 min. at as low a temperature as 500°C. or 600°C. , although the structures appeared to be identical in longitudinal sections (Figs. E-H, Plate CXXXIII).

The hardness data do not necessarily support the authors' theory that sintered platinum has a high temperature of recrystallization, for the data may have been affected by variations in grain-size. It is well known that the hardness of well-annealed brass can vary by nearly 100%, depending on the grain-size,† and it is reasonable to suppose that similar variations may occur in sintered platinum, for Smithells ‡ has stated that "grain growth in a pressed powder is similar to grain growth in worked metal and subject to the same general laws". Using an Eberbach micro-hardness tester, I have found that the hardness of sintered platinum does appear to vary with the grain-size. In a transverse section of a cold-drawn (92% reduction in area) sintered platinum wire which had been heated at 600°C. for 15 min., the micro-hardness number varied from 44 in coarse grains to 95 in fine-grain areas. The authors might have detected similar variations in hardness if they had used a micro-hardness tester, because one of their photographs shows both fine and coarse grains in a sintered wire after heating at 1200°C. (Fig. 4, Plate LXX).

The authors' statement that X-ray investigation confirmed the results of

* Research Laboratory, The International Nickel Co., Ltd., Bayonne, N.J., U.S.A.

† W. H. Bassett and C. H. Davis, *Trans. Amer. Inst. Min. Met. Eng.*, 1919, 60, 434.

‡ C. J. Smithells, "Tungsten", p. 72. London: 1936 (Chapman and Hall, Ltd.).

microscopic examination is not conclusive without further information. For instance, the reference to the appearance of spotted rings in the pattern of a wire heated at 1200°C . for 18 hr. might merely mean that the grain-size exceeded 5×10^{-3} mm. if Hull-Debye-Scherrer patterns were referred to, because there is a blind spot between 5×10^{-3} mm. and 2×10^{-4} mm. which would rule out this method for measuring the grain-size of the fine fibrous structure before grain growth had occurred.

The AUTHORS (*in reply*): We appreciate the interest which the paper has aroused and note with pleasure the broad agreement that exists with the general statement that "the increased stability of the fibrous structure of sintered platinum wire, as compared with similar wire produced from regular platinum, is attributed to a small amount of suitably dispersed porosity". It is satisfying to note too that the discussion has helped to elucidate some points which were not treated in detail in the paper.

Dr. Chaston mentions that he has never been able to get quite such persistent fibrous structures as are shown in our Fig. 4 (Plate LXX). This has also been the initial experience of other investigators, and it is readily explained by variations in the method of hot working which have the tendency to reduce the amount of porosity below that necessary to obtain the special properties of sintered wire. Sintering *in vacuo* also comes in this category, as it would naturally be assumed that a lower temperature would then have to be used in order to obtain the same amount of porosity in the compact as when sintering in hydrogen or any other gas. We are impressed by the results of Dr. Chaston's experiments involving "sheath-rolling", as this is an example of a procedure which might be adopted when it is required to obtain sintered metal with a minimum of porosity and which consequently does not possess a persistent fibrous structure and the associated properties which we have described.

Professor von Zeerleder has shown that special physical properties may be obtained in a base metal, namely in massive aluminium, which has been produced from powder. He expresses an opinion, with which we fully agree, "that these special properties of sintered powder compacts cannot be fortuitous, but must be of a quite fundamental nature". Perhaps Professor von Zeerleder would agree that the properties he has noted in the case of sintered aluminium have something in common with the oxide-containing platinum to which Dr. Dowson refers. Is it not likely that the inevitable oxide present in the aluminium plays a role comparable with that of the thorium in platinum? In answer to the question on increased hardness of wires at room temperature, we confirm that platinum wire produced by powder metallurgy has given a diamond pyramid hardness number of 126 compared with 94 for wire produced from the same platinum by the ordinary melting and casting procedure. We would agree that the crystallite theory of strength receives some support from the connection of special properties with the small particle size of the platinum powder, but do not consider that the structural dimensions have any direct relation to the atomic regions appertaining to the vacant-lattice-site theory.

We are glad that Dr. Dowson has taken this opportunity of outlining some of the interesting observations he and others have made on sintered platinum containing an inert solid phase such as thorium. The properties of this phase are such that it retains its identity during the sintering and subsequent hot working of the compact and does not coalesce or agglomerate, but remains as very small particles which are uniformly distributed throughout the metal. Clearly this confirms our suggestion "that the effect of finely dispersed porosity would probably be valid whether the pores were vacuous or filled with gas or with an inert solid phase".

With regard to the question about oxide films on platinum, the answer may be provided by the experiments described on the preheating of platinum powder in a stream of dry hydrogen, and by sintering and hot working the powder compact in a stream of the same reducing agent with the object of eliminating oxide films. The resulting wires from all of many experiments had the same properties as wires produced by sintering and hot working the platinum powder compacts in air.

We too have observed that sintered platinum sheet does not show enhanced properties to the same extent as wire produced at the same sintering and hot-working temperature. This we ascribed to the difference in stress distribution during rolling in open as compared with closed passes, and the resultant effect on porosity.

Mr. Atkinson has made a welcome addition to the investigation of columnar structures by making micro-hardness tests on transverse sections of sintered wires. We would like to add that in our paper, the term "high recrystallization temperature" was used in the conventional sense, to provide a simple exposition of the results given in Fig. 12, where hardness values are plotted against temperatures of heating for 15 min. In all cases, sintered platinum requires a higher temperature in order to produce complete softening as compared with ordinary platinum.

In conclusion, it would seem that a general characteristic of sintered platinum is an increased resistance to slip as compared with regular platinum. If this be due to suitably dispersed porosity then some comparison might be made of the character of this porosity as compared with other agents of slip hindrance, such as grain boundaries, age-hardening, and plastic deformation. The simplest picture of dispersed porosity is that of ultra-microscopic discontinuities in the metal lattice, which is fundamentally different from the picture of the transitional lattice of the grain boundaries, the distorted lattice of the age-hardened metal, and the fragmented lattice of the cold-worked metal.

CORRESPONDENCE ON THE PAPER BY MR. R. CHADWICK, DR. T. L. L. RICHARDS, AND MR. K. G. SUMNER: "THE EFFECT OF ROLLING AND ANNEALING PROCEDURES ON THE STRUCTURE AND GRAIN-SIZE OF ALUMINIUM-COPPER-MAGNESIUM ALLOY STRIP."

(*J. Inst. Metals*, this vol., p. 627.)

PROFESSOR PAUL A. BECK * : The effect of the rate of cooling from 500° C. previous to final rolling on the critical deformation is very interesting. On p. 638 the authors suggest that this effect may be exerted through a variation of the amounts of copper and magnesium in solid solution.

Since the critical deformation is the smallest deformation to cause complete recrystallization, its value strongly depends on the temperature used for recrystallization and on the time allowed at this temperature. For a given time and temperature of annealing, the critical deformation increases with a decrease in the rate of recrystallization. It has been observed † in precipitation-hardening lead alloys that the state of dispersion of the precipitate has a pronounced effect on the rate of recrystallization. A finer dispersion (larger number) of precipitate particles can slow down the recrystallization process considerably. Hence, it may be expected that the lower critical deformation value for the slowly cooled specimens may have resulted from an increase in the rate of recrystallization as a consequence of coalescence of the precipitate particles. On the other hand, the quenched specimens may have produced a very fine precipitate during deformation and final annealing, causing a decrease in the rate of recrystallization and a corresponding increase in critical deformation.

DR. M. HANSEN ‡ (Member): I have read this paper with considerable interest as, some years ago, we at the Research Laboratory of Dürerer Metallwerke A.G., Berlin, were very much interested in influencing the structure and grain-size of Duralumin deep-drawing sheets by varying the cold-rolling and heat-treatment procedures.

Earlier work on the recrystallization behaviour of commercial aluminium § and an aluminium-copper-silicon alloy || had shown that a medium-sized initial grain does not tend to become coarse on relatively small rolling reductions and subsequent recrystallization annealing. With a fine grain, this

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† P. A. Beck, *Trans. Amer. Inst. Min. Met. Eng.*, 1940, 137, 234 (author's reply to discussion).

‡ Senior Metallurgist, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill., U.S.A.

§ E. Wetzels, *Mitt. K.-W.-Inst. Metallforsch.*, 1922, 1, 24.

R. Karnop and G. Sachs, *Z. Physik*, 1927, 42, 283; 1928, 52, 301.

|| H. Bohner and R. Vogel, *Z. Metallkunde*, 1932, 24, 169.

treatment would result in a coarse grain structure due to "critical" reduction. In order to obtain a medium-sized grain in the finished sheet it was necessary to use an over-critical final reduction, between 15 and 25%.* Solution-annealing then resulted in a grain-size which remained practically unchanged on subsequent repeated deep-drawing and solution-annealing cycles. This method † was used in the manufacture of deep-drawing sheets of aluminium-copper-magnesium alloys. However, it has the disadvantage that it makes necessary the abandonment of high final reductions, which are desirable in large-scale production.

In contrast to Duralumin sheet, we have never observed that Duralumin strip tends to become coarse grained when subjected to repeated critical deformation and solution-annealing cycles. Further, it was found that strip always had the favourable medium grain-size after solution-annealing in spite of a high final reduction, whereas sheet had a fine-grained structure. This difference in structure is due to the fact that the hard-rolled strip coil is given an annealing in an air furnace at about 350° C. before solution-annealing in the salt bath in order to reduce the tightness of the windings.

Further investigation has shown also that Duralumin sheets, in spite of high final reductions, become immune to coarse-grain formation on repeated critical deformation and recrystallization if the hard-rolled sheets are subjected to a short-time "pre-annealing" in a salt bath at temperatures between 300° and 350° C. before being transferred to the salt bath for solution-annealing treatment.‡ This confirms the observations by the present authors that rapid heating resulted in a finer grain-size than slow heating in air, and also that "for rolling reductions of 50 and 75% the only factor which appeared to have any significant influence on grain-size was the rate of heating in the final heat-treatment".

Based on the facts given above, a method of producing deep-drawing Duralumin sheets has been developed, details of which are given elsewhere.§ The annealing temperature and time of the "pre-annealing" treatment depend upon the final degree of rolling reduction and the manganese content of the alloy in such a way that the structure after "pre-annealing" should be just recrystallized, preferably partially recrystallized.

In addition, I would like to refer the authors to the predominant influence of manganese on the recrystallization behaviour of aluminium-copper-magnesium alloys.|| For instance, the critical degree of deformation of an alloy with the basic composition copper 4.2, magnesium 0.83, iron 0.23, and silicon 0.15% is increased from 4% with 0.2% manganese to 15% with 0.6% manganese. According to our work, it seems probable that greater differences in grain-size would have been obtained by varying the rolling and annealing procedures if the authors had used in their experiments an alloy having a manganese content smaller than 0.6%.||

The AUTHORS (*in reply*): We agree with Professor Beck that the state of dispersion of a precipitate might have a pronounced effect on the rate of

* M. Hansen and G. Moritz, *Aluminium*, 1941, 23, 14, 81.

† M. Hansen, *FIAT Rev. German Sci.* 1939-1946: *Non-Ferrous Metallurgy*, Part I, 1948, p. 111.

K. Matthaes, *Lilienthal Ges. Luftfahrtforsch., Rep.* A49/3, 1938; E. Lay and A. Grimm, *Aluminium*, 1938, 20, 859; C. H. Schröter, *Aluminium*, 1939, 21, 589; A. Schroeder and K. Matthaes, *Metallwirtschaft*, 1941, 20, 631; *Aluminium*, 1941, 23, 599.

‡ K. L. Dreyer and M. Hansen, *Z. Metallkunde*, 1942, 34, 121.

§ K. L. Dreyer and M. Hansen, *loc. cit.*

M. Hansen, *FIAT Rev.*, *loc. cit.*

|| K. L. Dreyer and M. Hansen, *Z. Metallkunde*, 1941, 33, 193; 1942, 34, 121.

recrystallization, and without further experimental work it is not possible to decide whether this is more significant than the solute content of the matrix. It is also possible that the process of precipitation, where this occurs during annealing, influences recrystallization behaviour.

We were aware of the information published by Dr. Hansen and his co-workers on the methods of controlling grain-size, and indeed our own work began with an attempt to confirm these results. The omission of systematic data from the papers dealing with Duralumin, and the considerable difference in composition from our own material, to which Dr. Hansen has drawn attention, make comparison with our results difficult. We could find no evidence, however, of the efficacy of either the "pre-annealing" treatment or the overcritical final reduction. Moreover, we find it difficult to explain Dr. Hansen's observations in terms of our own experimental results on the rolling and annealing of aluminium alloys.

We realize that manganese has probably an important influence on the recrystallization behaviour of aluminium alloys generally, and indeed its effect in increasing critical reduction and thus restricting coarse-grain formation in a non-heat-treatable alloy has been reported by one of us,* while in the paper under discussion we suggested (p. 638) that the high critical-reduction values observed might be associated with the presence of manganese. Dr. Hansen's information on this point is therefore most welcome and confirms our views.

* R. Chadwick and W. H. L. Hooper, *J. Inst. Metals*, this vol., p. 609.

CORRESPONDENCE ON THE PAPER BY DR. W. BETTERIDGE, DR. C. WILSON, MR. M. A. HAUGHTON, AND MR. W. MORGAN: "THE INFLUENCE OF OVER-AGEING AND ANNEALING ON THE HARDNESS AND MICROSTRUCTURE OF AN ALUMINIUM ALLOY TO BRITISH STANDARD SPECIFICATION L42."

(*J. Inst. Metals*, this vol., p. 641.)

MR. T. H. SCHOFIELD,* M.Sc., F.I.M. (Member): In connection with some work carried out at the National Physical Laboratory for the Ministry of Aircraft Production in 1940-41 on the possibilities of estimating piston temperatures by means of hardness measurements, the effect of time and temperature of heating on the hardness of forged R.R. 59 (B.S.S. L42) alloy was investigated. It was observed that the amount of age-hardening at room temperature after heating at 350° C. depended on the time of heating, and it was pointed out that it would be necessary to take this effect into account when estimating piston temperatures from hardness measurements. The effect of time of heating at 250° and 350° C. on the hardness both before and after ageing at room temperature is shown in Table A.

Thus, although the degree of softening after heating both at 250° and 350° C. depends on the time of heating, no significant recovery in hardness after ageing for six months occurs after heating for periods up to 652 hr. at 250° C., but the amount of age-hardening after heating at 350° C. depends on the time of heating, being appreciable with short periods of heating and insignificant with long periods. It follows that the amount of age-hardening does not depend on the hardness immediately after softening; for example, the hardness of specimen 5913 (70½ hr. at 250° C.) has substantially the same hardness as that of specimen 5912 (½ hr. at 350° C.). This suggests that the mechanism of softening depends on the temperature and time.

In further work carried out in 1942-43, to which reference is made in the authors' paper, the effect was further investigated on certain other aluminium-base alloys including, besides R.R. 59, Duralumin, aluminium-4% copper alloy, and two exploratory piston alloys developed by the Royal Aircraft Establishment. Specimens 2 cm. long, 1.5 cm. wide, and 0.5 cm. thick were cut from forged and fully heat-treated material and heated at temperatures between 125° and 500° C. in intervals of 25° or 50° C. for periods of 1, 16, and 256 hr. (and in some cases for 4, 64, and 128 hr. in addition). The Brinell hardness (2 mm. ball, 250 kg. load, applied for 15 sec.) of each specimen was measured immediately after air cooling and after intervals of 3, 10, 30, and 90 days at room temperature. Unfortunately, owing to the *ad hoc* nature of the investigation and to the pressure of other work, it was not possible to carry out a microscopical and X-ray examination

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TABLE A.—Effect of Time and Temperature of Heating on the Softening and Subsequent Age-Hardening of R.R. 59 (B.S.S. L42) Alloy.

Number of Specimen	Time of Heating at 250° C., hr.	Brinell Hardness at Room Temp. (5/250/15)		
		Immediately after Heating	Six months after Treatment	Change in Hardness
59	Not reheated	128	127	— 1.0
5914	2	114	115	+ 1.0
5917	5½	106	107	+ 1.0
5916	14½	91.8	95	+ 3.2
5915	24	81.3	83.9	+ 2.6
5913	70½	62.7	62.4	— 0.3
5918	98	59	58.4	— 0.6
5921	145	56.3	56.3	0
5922	652	53.8	52.3	— 1.5
	Time of Heating at 350° C., hr.			
5912	½	61.2	77.9	+ 16.7
5910	1	60.6	73.9	+ 13.3
599	2	58.4	72.4	+ 14.0
591	5	54.5	64.2	+ 9.7
592	24	50.5	57.9	+ 7.4
5911	66	44.4	48.3	+ 3.9
5919	97	41.2	45.1	+ 3.9
5920	648	38.3	37.7	— 0.6

of the specimens, but the results agree substantially with the authors' over the range of time and temperature in which comparison can be made. It is gratifying to note that the authors have been able to examine the problem more thoroughly and to put forward a working explanation of the inflection in the hardness/temperature curve.

Further attention might, however, be given to the results obtained by the writer on the effect of time and temperature on the subsequent age-hardening at room temperature, as mentioned in the first part of this discussion. Fig. A shows the effect of time and temperature on the age-hardening at room temperature of R.R. 59 (B.S.S. L42) alloy after heating at 375° and 450° C. At both temperatures longer times of heating result in less age-hardening, but the difference in the amount of age-hardening between corresponding times of heating is less after heating at 450° than at 375° C.

Fig. B shows how the amount of age-hardening (i.e. the difference between the hardness immediately after heat-treatment and that after ageing for 90 days at room temperature) varies with the time of heating at temperatures between 300° and 500° C. It appears that the ultimate amount of age-hardening is of the same order after various periods of heating, but that the ability to age-harden after softening begins at higher temperatures and reaches a maximum at higher temperatures with longer periods of heating.

Similar results, though different in degree and in temperature range, were obtained with the other complex alloys investigated, but the results obtained on pure aluminium-4% copper alloy were different. Thus, no age-hardening occurred after short periods of heating even at 450° C. (Fig. C) and, in contrast to the results obtained on R.R. 59 and the other complex

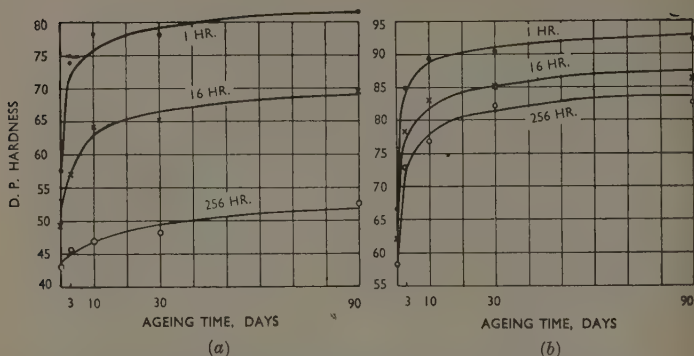


FIG. A.—Effect of Time of Heating at (a) 375° and (b) 450° C. on the Subsequent Room-Temperature Ageing of R.R. 59 Alloy.

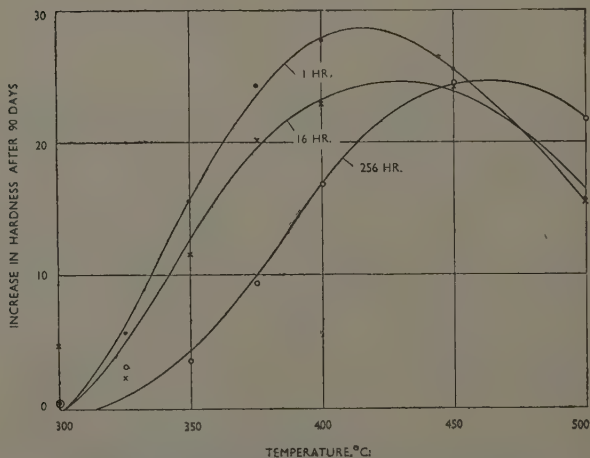


FIG. B.—The Effect of Time of Heating at Various Temperatures on the Room-Temperature Age-Hardening of R.R. 59 Alloy.

alloys, heating at both 450°C . and 500°C . for long periods resulted in greater age-hardening than heating for short periods (Fig. C (a) and (b)). These results are what might be expected, since the solubility of copper in aluminium begins to increase rapidly with temperature at about 430°C ., and in a binary alloy the amount taken into solution would be expected to increase with

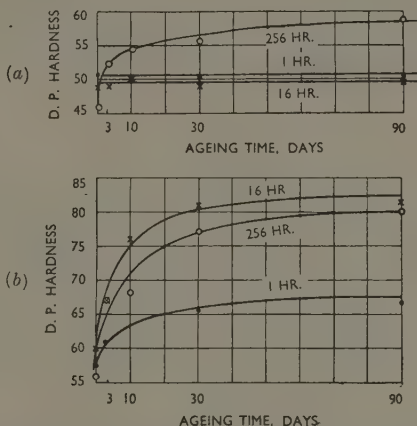


FIG. C.—Effect of Time of Heating at (a) 450° and (b) 500°C . on Subsequent Room-Temperature Ageing of Aluminium-4% Copper Alloy.

time. The age-hardening of the complex aluminium alloys containing copper, magnesium, and silicon (such as R.R. 59), however, is due both to Mg_2Si and CuAl_2 , and it appears that the ability of these alloys to age-harden after softening is influenced by the composition of the solid solution and possibly also by the presence of other constituents. A precise explanation of the results cannot therefore be given without more detailed study.

The AUTHORS (*in reply*): We are grateful to Mr. Schofield for his communication and are pleased that he confirms that our results are substantially in agreement with his own. Curves corresponding to those in Fig. A (a) plotted from our results for annealing periods of 4, 20, 50, and 100 hr. lie in suitable relation to Mr. Schofield's curves for periods of 1, 16, and 256 hr. Similarly, curves corresponding to those of Fig. B could be plotted from our results for temperatures up to 400°C ., although it is not felt that such plots of hardness increments are as useful as those of absolute hardness values.

The observation that the behaviour of the simple aluminium-copper binary alloy is different from that of the complex alloys should be helpful in developing a more complete explanation of the phenomenon, but the results which Mr. Schofield has submitted are not sufficient evidence in themselves, particularly since they relate to an annealing temperature of 450°C . which is approaching the temperature for complete solubility. It would be interesting to know whether this alloy shows an inflection of the hardness/temperature curve after annealing and ageing at room temperature, for, if it does, it would provide further evidence that the phenomenon is not due to the precipitation of an additional phase but to some effect of incomplete annealing.

CORRESPONDENCE ON THE PAPER BY DR. V. KONDIC AND MR. H. J. KOZLOWSKI: "FUNDAMENTAL CHARACTERISTICS OF CASTING FLUIDITY."

(*J. Inst. Metals*, this vol., p. 665.)

DR. E. W. FELL * (Member): I am interested in the flow of molten metal in moulds, and I have read with much interest the authors' paper, in which they give considerable prominence to viscosity, though they refer to a somewhat conflicting and widely-held view that viscosity is of only minor or secondary importance. I should like, however, to discuss the subject of "casting fluidity" in a general way and from an angle which enables the chief characteristics of casting fluidity to be truly assessed and placed in order of real significance. To this end, only pure metals and their alloys need be considered at present.

The natural fluidity of molten metals, which is high and which therefore will be the predominant factor, is undoubtedly the most important fundamental characteristic of all those connected with casting fluidity. The viscosity of iron and of non-ferrous metals is low and it exerts, therefore, only a proportionally small influence on the natural fluidity.

I would place the heat content of the molten metal as second in order of importance, because of its great influence in the mould cavity in association with the natural fluidity of the molten metal. Viscosity comes third in order of importance. The above remarks refer, especially, to the length of the spiral casting obtained with the mould as used by the authors, and it is also proper to give priority in the order of importance to the properties of the melt.

Regarding viscosity, Table I of the paper shows that, although viscosity has a considerable influence on the casting-fluidity values, as would be expected, the most important characteristic of the casting fluidity is the more abstract natural fluidity. Thus, molten lead has incidentally the highest viscosity given in the Table, but if it can flow a distance of 42 in. along a circular channel only $\frac{1}{4}$ in. in dia., the temperature of the metal being only 25° C. above its melting point, then there must be a more important fundamental characteristic of casting fluidity than the viscosity. Regarding the authors' use in Table I of the term "absolute fluidity", it would be better to give the viscosity instead of the absolute fluidity, for the reciprocal of the viscosity is of doubtful significance as far as casting fluidity is concerned.

In practice, when the mould cavity is wide and not very long, viscosity is of no importance if the making of a casting be taken to comprise two stages: (a) the filling of the mould with molten metal, and (b) the subsequent freezing process resulting in flow of molten metal due to volume shrinkage, and provided that stage (b) is left out of discussion and ignored because of narrow channels between the parts already frozen. Similarly, the heat content per unit volume would be unimportant because a wide section of molten metal means a greater total heat content. Thus glycerol at room temperatures, to take a simple example, is a liquid whose viscosity is about three hundred times greater than that of molten lead, but which would flow into and fill a mould

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cavity easily if the cavity had broad dimensions. Here too, for glycerol, the natural fluidity remains a most important characteristic. Thus, to the foundry metallurgist, the value of the information afforded by the "casting-fluidity" test depends to a considerable extent on the size and shape of the particular cavity to which the information is to be applied. To take perhaps a possibly extreme example, if the mould cavity resembles the cavity employed in the test then the information it affords will be particularly appropriate.

There appears to be an error in the units used in the paper. The unit of viscosity is the poise, and it is incorrect therefore, in Fig. 6 and Table I, to express absolute fluidity in poises. Absolute fluidity may be suitably expressed as a number on the C.G.S. scale.

The AUTHORS (*in reply*): We wish to thank Dr. Fell for his contribution. We cannot, however, agree with his interpretation of "casting fluidity". As this is an entirely empirical conception, the conditions under which it is defined must be unequivocally stated. For the purpose of our paper, the definition was based on the flow of molten metal in a narrow channel. A broader definition, covering the flow of metals in moulds, is also used, but is much more difficult to interpret quantitatively. In Dr. Fell's qualitative assessment of factors that affect casting fluidity (he used the second definition), the "natural fluidity" is considered to be the most important. We fail to see what is meant by that term. We believe that casting fluidity (according to the first definition) can be interpreted quantitatively and qualitatively in standard physical terms. If the second definition is used, we maintain that the same factors operate, but that any quantitative interpretation is impossible.

CORRESPONDENCE ON PAPER BY DR. H. K. HARDY : "MODERN DESCRIPTIVE THEORIES OF PRECIPITATION PROCESSES."

(*J. Inst. Metals*, this vol., p. 707.)

DR. WALTER L. FINLAY * (Member): Dr. Hardy has presented a lucid exposition of present thought regarding the mechanism of precipitation from solid solution. The writer wishes simply to add two footnotes for completeness:

(1) Dr. Hardy cites his reference 34 in stating that the phenomenon of reversion occurs principally in aluminium-copper and Duralumin-type alloys, and that it occurs only to a much lesser extent in other systems. Recently, it has been shown that aluminium-zinc alloys show a very marked reversion.†

(2) In discussing the marked inhibition of subsequent rehardening after reversion, Dr. Hardy remarks that no explanations have been offered for this effect. Guinier ‡ has ascribed the reduced hardening rate of the retrogressed structure to the absence of the high internal stresses in it (and, therefore, of the many lattice defects which promote nucleation of precipitate particles) which are present as a result of quenching stresses in the as-quenched alloy.

The AUTHOR (*in reply*): I am pleased that Dr. Finlay has added the note about the paper of which he is joint author. I had made a mental note to include the information when proof reading, but I am afraid that the intention proved superior to the deed. I quite agree that aluminium-zinc alloys show an appreciable reversion effect.

Saulnier§ has recently suggested that the particles initially present over-age during reversion to the stage corresponding to the flat portion on Gayler's ageing curves. He puts forward the view that the reverted material has the same hardness as specimens aged, immediately after quenching, to the "flat" at the reversion temperature. On this supposition the slower re-ageing is due to depletion of copper.

Work by Lacombe and Berghézan || prompts the thought that there might be a change in the dislocation distribution during the reversion process which would account for slower re-ageing. This aspect of precipitation theory is at a very interesting stage of development, and I feel that only future experimental work will decide between the different possibilities. Any theory of reversion must be capable of explaining why re-ageing is slower when only partial reversion has taken place than after full reversion. This factor is not easily accounted for by theories based on over-ageing or release of micro-internal stresses.

* Supervisor, Metals Research, Remington Arms Company, Inc., Bridgeport 2, Conn., U.S.A.

† W. L. Finlay and W. R. Hibbard, Jr., *Metals Technol.*, 1948, **15**, (6); *A.I.M.M.E. Tech. Publ.* No. 2470.

‡ A. Guinier, *Research*, 1949, **2**, 6.

§ A. Saulnier, *Rev. Aluminium*, 1949, (157), 235.

|| P. Lacombe and A. Berghézan, *Compt. rend.*, 1949, **228**, 1733.

DISCUSSION ON PAPER BY DR. W. I. PUMPHREY AND MR. D. C. MOORE: "SOME EFFECTS OF SILICON ON THE TENDENCY TO CRACKING IN ALUMINIUM-COPPER-MAGNESIUM ALLOYS OF HIGH PURITY."*

(*J. Inst. Metals*, this vol., p. 727.)

DR. E. G. WEST* (Member): This further contribution from Dr. Pumphrey and his colleague goes a little further towards the completion of the work which was started some five years ago and which has been presented to this Institute in a series of papers. It marks a further advance in what may be called the "synthesis" stage of this programme, as against the "analysis" stage which occupied the first period of the programme. This paper describes the effects of deliberate additions of silicon in an attempt to reduce the incidence of cracking or hot tearing in welded joints.

It is interesting that the authors mention in their reference to previous work, the value of additions of silicon to an aluminium-copper-magnesium alloy reported by an American author in 1946. That type of alloy was developed in this country, by the late Percy Pritchard, in 1939-40 to use up scrap aircraft material, and became very well known as D.T.D. 424. I think that this has not been generally published, but it is worth putting on record, especially as it indicates the value of the silicon additions. These additions do, however, tend to give rise to difficulties of other kinds, particularly in the heat-treatment of these alloys, and it may not be practicable to produce welding-quality Duralumin-type alloys with these high silicon contents.

I would draw attention to a remark in the paper which is indicative of the value of work of this kind being carried out in a university laboratory, but closely associated with industrial metallurgists concerned with the problems in question. On p. 732 it is stated that certain alloys are difficult to weld, and although the authors do not say just what the difficulties were, the following up of such observations by trained investigators is, I am convinced, an excellent way to elucidate practical problems which baffle the metallurgist. Perhaps the authors could say why these alloys were difficult to weld, and indicate what steps have been or are being taken to get over those particular practical difficulties.

DR. W. I. PUMPHREY (*in reply*): In welding the alloy containing magnesium 4, copper 4, and silicon 0.5%, when the welding torch played on the abutting edges of the sheets of this alloy, the edges melted, but at once became covered with an irregular black film, which prevented the molten edges from running together, and, even when the joint was well fluxed, it was found impossible to avoid the trouble. The cause of the black film on the surface is not known, since its occurrence has not been observed in any other of the aluminium-copper-magnesium-silicon alloys, but we are working on this problem, because it is associated with a number of other film problems which we have observed in welding. At present, however, we have no precise answer to the problem.

* Discussion at the Annual Autumn Meeting, Paris, 4 October 1949.

† Technical Director, The Aluminium Development Association, London.

CORRESPONDENCE ON PAPER BY DR. D. E. ADAMS : " SEGREGATION IN ALUMINIUM-COPPER ALLOYS."

(*J. Inst. Metals*, this vol., p. 809.)

DR. V. KONDIC * (Member): The phenomenon of segregation before or during solidification belongs to the large group of metallurgical phenomena, the importance of which arises from the industrial uses of alloys. Consequently, a large proportion of the investigational work on this phenomenon has been, in the past, more concerned with ways and means of overcoming certain forms of segregation which are particularly detrimental in alloy applications, rather than with the question of explaining the nature and mechanism of segregation. A great amount of effort was expended in this way in collecting the data about segregation, before any complete theory could be put forward that would account for the results observed. Even to-day, certain aspects of segregation are not explained, mainly owing to the semi-empirical nature of the methods used in the experimental work.

It is therefore most gratifying to find that the work presented in this paper is a positive contribution to the fundamental studies of the segregation problem. There is very little that the work lacks on the experimental side. For further analyses, future researches, and the interpretation of existing results, it would be helpful to have the following additional information: (a) It is not made clear in the paper whether the metal was melted in a separate furnace, and if so, what were the temperatures of molten metal, mould, and chill plate before pouring. Was the superheating temperature controlled? (b) Was there any eutectic exudation in the two very slowly cooled ingots? (c) What was the residual amount of titanium in grain-refined alloys, and were the undercooling characteristics of this alloy in any way different from those of untreated alloys?

The data provided in the paper give additional evidence in support of the interdendritic-flow theory of inverse segregation. Whilst this theory is now generally well established, certain of its aspects still remain obscure. It is in this field that it becomes difficult to accept the author's interpretation of the results obtained. Two major points arise in this connection.

The existence of a temperature gradient during solidification is one of the fundamental conditions for the appearance of segregation. Such gradients can be readily measured. The problem of concentration gradients of solute atoms within the liquid of the solidifying (pasty) zone is a much more difficult question. The existence of concentration gradients, such as suggested by the author (Fig. A) cannot be, however, readily accepted. First of all, it is not clear whether the suggested mean composition within the solidifying zone is that of the liquid alone or of the mixture of the liquid and solid? Be that as it may, the schematic representation of crystal growth, reproduced in Fig. A (a), gives a wrong impression of the mode of solidification of liquid solutions. In fact (see Fig. A (b)), the growth of crystals in this case is almost equally fast laterally, so that the side branches of growing dendrites soon lock together enclosing, partly or completely, the solute-rich liquid. The mean composition,

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in the case of unidirectional solidification, at any horizontal cross-section in the pasty zone, as the author's results show, is constant and equal to the composition of the liquid alloy. Concentration gradients exist essentially on a micro-scale, and the effect of solute-rich liquid flowing in the direction of solidification does not alter the average composition along the vertical axes of the ingot. This process is continuous and balanced, so that liquid flowing out from any layer is replaced by an equivalent amount of liquid of similar composition during subsequent solidification.

An important question thus arises: What are the reasons for the existence of an exuded (solute-rich) layer at the bottom and sides of ingots and why is the top part impoverished in the solute? The latter question, as suggested by the author, can be readily explained by the lack of feeding liquid during the last stages of solidification. The author then suggests that the main condition for the existence of an exuded layer at the chill face is the formation of an air gap, between the solidifying ingot and the mould face (evidently owing to contraction effects), into which solute-rich liquid exudes, the determining driving force being that of capillarity (surface energy). This explanation is very doubtful. While further experimental work is required to provide an adequate explanation of this particular phenomenon, two interesting factors have already been established, neither of which was mentioned by the author. Firstly, the outflow of solute-rich liquid follows very closely the pattern of solid contraction stresses. For example, in a cast billet for rolling, the areas showing the greatest extent of exudations are the side edges and the central portion of the ingot surface. Secondly, it has been shown by Sauerwald * that the type of volume changes during solidification of a solid solution is closely related to the tendency of an alloy to exhibit the exudation type of segregation. While it is difficult to see how the effect of capillary forces could be experimentally checked, the evidence already available about the part that the contraction stresses and volume changes, during solidification, may play in relation to exudations, should not be overlooked.

The AUTHOR (*in reply*): The first point raised by Dr. Kondic in respect of the suggested mechanism of segregation concerns the concentration gradient in the solidifying layer. The presence of inverse segregation at the chill face is established; thus, if it is agreed that mass diffusion within the liquid is slow relative to the speed of cooling, there must be a region of diminished composition in the solidifying zone to make the composition integrated along the length of the ingot equal to the mean composition. The experimental results do not demonstrate, as is implied by Dr. Kondic, that the composition during solidification at any horizontal cross-section is the mean composition of the alloy.

Too literal an interpretation has been adopted of the parts of the diagrams symbolizing the solidifying zone; the illustrations were not intended to convey the idea of crystals growing in a conical form, but only that there is a layer of mixed solid and liquid, varying from all solid at the bottom to all liquid at the top.

A reference to exudations is the other main point in Dr. Kondic's com-

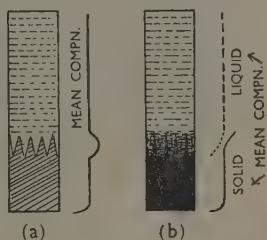


FIG. A.—Adams's (a) and Kondic's (b) Representation of the Pasty Zone During Solidification.

* F. Sauerwald, *Metallwirtschaft*, 1943, 22, 543.

ments. It is clear from results quoted in the paper, and from other work, that exudations are to be expected when a gap is formed between the mould face and the solidifying ingot. The force which causes liquid to flow into such spaces was not specified, and the experiments were not directed to clarifying this point; contraction stresses may well be the determining factor in some cases. The role of solidification contraction is, of course, vital to the appearance of inverse segregation and may be expected to give a predisposition to exudation at a chill face. In non-directionally cooled ingots the release of gases may force liquid into any space between the mould and the solidifying ingot.

In reply to the request for further information, it may be said that the mould, including chill face, and the alloy (melted in another crucible before pouring) were preheated to a temperature well above the melting point. No examination was made for exudations on the very slowly cooled ingots and no estimation of residual titanium in the grain-refined alloy was made in view of the absence of any marked difference in its behaviour during cooling or in its segregation.

CORRESPONDENCE ON PAPER BY ING. J. SCHOOF: "NOTE ON A PARTICULAR TYPE OF COLD WORKING OF GRAINS OF α -BRASS BY ROLLING."

(*J. Inst. Metals*, this vol., p. 855.)

MR. J. B. HESS* and DR. C. S. BARRETT*: There is a fundamental objection to the author's tentative conclusion that the white bands in Figs. 1-4 (Plates CX and CXI) are mechanical twins. If they were twins, the crystal lattice within the bands would have an orientation identical with that of some of the annealing twins already present, and would, therefore, be expected to etch in like manner. But such similar etching is not observed. On the contrary, the bands are said to be invisible after chemical etching that presumably was adequate to reveal annealing twins.

The basic premise that the white bands are associated with one of the composition planes of previously existing annealing twins could easily be tested by re-etching an area which contained the white bands with an etchant that clearly reveals annealing twins. Similarly, a longitudinal section through such an area would neatly verify or disprove the hypothesis that the white bands occur in those twinned grains in which the composition planes are both perpendicular to the plane of the sheet and to the rolling direction. Have such experiments been conducted?

The AUTHOR (*in reply*): Mr. Hess and Dr. Barrett consider that if the bands have an orientation with respect to the plane of the sheet identical with that of the rest of the grain, as I have supposed, they should be of the same colour after attack. I believe that the formation of mechanical twins involves a certain degree of cold work, and that it is the latter which leads to the difference in appearance. Indeed it can be shown that in other grains which do not exhibit white bands, certain irregular zones are attacked differently from the rest of the grain; these zones, although not showing slip lines, are normally situated in such a part of the grain that it is evident that the degree of cold work there is different.

Chemical attack after electrolytic polishing does not enable the white bands to be seen, though it can be observed that in the grains concerned a trace on two of the twinning planes is less clear. Nor does chemical attack after short-circuit etching permit the phenomenon to be observed any better, for the attack must be severe in order to dissolve the deposit formed during short-circuit etching.

Examination of a longitudinal section would clearly be a certain method of testing the hypotheses put forward, but such an examination is not possible owing to the small number of grains exhibiting the phenomenon and their small dimensions. It can, however, be said that on repeating the polishing on the same specimen, the width of the white bands decreases as well as the number of grains displaying them; this supports my hypothesis, according to which it is the obliquity of the rolling force which gives rise to the phenomenon (Figs. A and B, Plate CXXXIV).

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JOINT DISCUSSION ON PAPER BY MM. J. MATTER AND M. LAMOURDEDIEU : " THE NEW FACTORY OF THE SOCIÉTÉ CENTRALE DES ALLIAGES LÉGERS AT ISSOIRE (PUY-DE-DÔME) FOR THE WORKING OF LIGHT ALLOYS "; AND ON PAPER BY MR. W. J. THOMAS AND MR. W. A. FOWLER ON " SOME TECHNICAL PROBLEMS INFLUENCING PRODUCTION ECONOMY IN THE ROLLING OF ALUMINIUM. " *

(*J. Inst. Metals*, this vol., pp. 899, 921.)

MR. W. J. THOMAS, introducing the paper by himself and Mr. Fowler, said : When it was suggested that a paper might be submitted dealing with some of the practical aspects of aluminium fabrication, we reviewed the various sections in which we had some experience to see which we thought would offer the greatest scope. We came to the conclusion that the rolling of the metal would be of the most interest, as the volume of production in this form exceeds all the other forms put together, and in recent years there have been more developments in plant and procedure. It was also thought that some notes on the production aspects would be a complementary contribution to the paper describing the large and very important new works at Issoire.

Developments in rolling procedure have been brought about chiefly by the introduction of large strip mills, which roll in heavy unit weights, and these have effected considerable improvements and economies, but it is suggested that there is still much to be done in order to get the maximum benefits from these new mills. A larger amount of standardization in regard to both sizes and the alloys dealt with would effect appreciable savings, but technical and plant problems are probably of even greater importance.

It would be difficult to get a yardstick which would indicate clearly how the efficiency of producing rolled products in light metals compares with that in steel or the other non-ferrous metals; there is such a wide range in each group. There is one pointer, however, in regard to the comparison with steel, inasmuch as the percentage recovery from the rolling slab in light metals is, I believe, generally lower, and this is particularly the case in the stronger light alloys. One of our main endeavours, therefore, should be to find a means of increasing the recovery.

Some of the technical problems still before us have already been with us for a long time; others are relatively new, being associated with the use of the more modern type of plant and the continuing demand for metal with ever

* Discussion at the Annual Autumn Meeting, Paris, 4 October 1949.

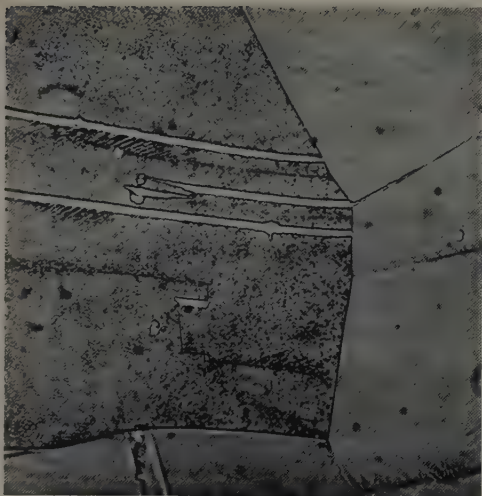


FIG. A.—Presence of bright bands in a grain after electrolytic polishing and short-circuit etching. $\times 500$.

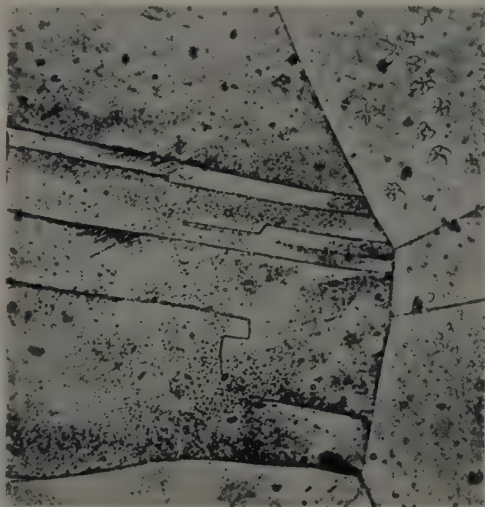


FIG. B.—Same field as Fig. A, but after a second electrolytic polishing treatment and etching in acid FeCl_3 . The bright bands do not appear. The second polishing has slightly displaced the grain boundaries in relation to the twinning planes. A third electrolytic polishing treatment followed by short-circuit etching resulted in a similar appearance to that shown in Fig. A.

[To face p. 1166.]

better properties. In describing some of these problems, which we believe are fairly general, we have ventured to give some opinions on the causes of the difficulties and how these might be dealt with.

The light alloy fabricating industry has in the past been very largely a closed shop. It is thought that we have not had the benefit of the same amount of collaboration as has obtained, for instance, in the steel rolling industry. All producers will obviously guard certain features of their technique, but there are many fundamental problems common to all, from the solution of which the industry as a whole must benefit, and it is hoped that this paper will provide some small contribution to that end.

MR. D. F. CAMPBELL,* M.A. (Member of Council): It is fitting, I think, that these two informative and provocative papers should be discussed in this fair city of Paris, because the European aluminium industry owes so much to France. The name of the ore comes from the village of Les Baux, in the South of France, and French metallurgists and chemists were largely responsible in the early days for the development of this metal.

I should like to say a few words about a very great French metallurgical genius, with whom I had the privilege of working for several years, not only by the torrents in the high alps of Savoy, but also by the rivers and lakes of Sweden, in California, in Chicago, and in North Carolina. I refer to Paul Héroult.

You all know the story of aluminium, first discovered by Wöhler and manufactured on a small scale by Henri St. Clair Deville, who produced aluminium for about thirty years. It was sold at about £2—in those days, two gold sovereigns—per pound of metal, and world production reached in due course a few tons a year. Then, in 1886, there was the remarkable fact that two young men of 23 discovered a new method of making aluminium, and discovered it simultaneously and independently, in France and in America.

Some of the stories which Paul Héroult told me of his early days are interesting and have never been recorded, so that it may be worth while to mention them. In all the history of industrial metallurgy, I do not believe that any man has done so much in developing metallurgical processes as Paul Héroult, though little has been written about his work and not very much is generally known; but throughout the world—in France, Sweden, England, and America—there are many monuments to his work.

In the early days, Héroult's experiments were carried out a few miles from Paris, at Gentilly, and later, aluminium was made at Froges and La Praz. Héroult's father had a very small Gramme dynamo, and he told me that at week-ends he used to experiment whenever he could get the dynamo, and he made a very small quantity of aluminium—about the size of an egg—with two friends, Merle and Dreyfus. At the time, nobody knew what to do with aluminium when they had made it. It was then worth £2 a pound; but within ten years the price went down to about 1s. 2d. a pound. (I am speaking of the days when gold was worth 85 shillings an ounce.)

Then came the period when there was plenty of aluminium but nobody knew of a use for it. Héroult was in great financial difficulties, but succeeded in getting some support from Neuhausen, and his friend Dreyfus helped him to establish himself. He built the works at Froges, where a substantial amount of aluminium was produced which was used for kitchen utensils and other purposes, and Héroult emphasized the importance of cheap aluminium, and one of his very few published articles was entitled "*L'Aluminium à bon marché*".

After completing his work on aluminium he turned to steel, and there are

* Chairman, Electric Furnace Co., Ltd., Weybridge, Surrey.

many monuments to his work in the iron and steel trade. He demonstrated very clearly the manufacture of pig iron from iron ore, and at Sault Ste. Marie made a ton of iron with 2500 kWh., which is hardly surpassed by the most modern furnaces in Norway and Sweden. He demonstrated the fact that iron could be made from iron ore, and he developed a furnace for the manufacture of steel; and to-day there are more than 1000 Héroult furnaces in the world, making more than 8,000,000 tons of steel. That is a testimony to the genius of this man, who did so much for industrial metallurgy.

In those days the making of aluminium was not a simple matter, because there were so many problems, such as the manufacture of electrodes, which involved a great deal of work, in addition to the development of the electric furnace.

The papers under discussion show that there is a vast production of aluminium to-day. It is the commonest metal on the surface of the earth. It is, of the non-ferrous metals, the one which has the greatest volume of production in the world, and it is going ahead very fast.

In addition to all the metallurgical work that Héroult did, he was a great civil engineer, and the power stations that he built are also monuments to his memory. Many of these power stations were built with very simple supervision. The power station at La Praz was built, he told me, very largely to sketches made on the marble tops of tables at the Café du Pont at La Praz, when he discussed the next day's work with his foreman mason. He was a man of very simple character, who knew what to do and was very quick at making decisions, but he hated red tape, and if he had lived to-day he would have loathed all the paper-work and forms and government control from which we are suffering both in France and Britain.

The aluminium industry is only sixty years old, and it is interesting to see how we are applying much of the technique of the steel trade to aluminium. I refer, of course, more especially to the strip mills and much of the equipment for the handling of large coils and strips described in these papers. I fully appreciate the difference between aluminium and steel, but now that the veil of secrecy which impeded progress in the aluminium industry for so long has been thrown aside we are all working together for the development of very heavy machinery for the rolling of aluminium and borrowing all we can from the experience of the steel trade.

The first of these papers gives in unprecedented detail the facts about a magnificent installation which will be the most important light alloy rolling mill in Europe, and the second is also, to my mind, exceedingly valuable. The latter is a provocative paper, which puts fairly and squarely before engineers and furnace builders the outstanding problems which they want us to solve. From the variety of equipment which is seen in aluminium works to-day there is undoubtedly much to be done. We do not really know what is the best furnace for the different operations of remelting, and I should like to ask MM. Matter and Lamourdedieu whether they can give us further information as to what, in their view, are the relative merits of high-frequency and low-frequency induction furnaces of various types with single or double metal baths, and of resistance furnaces of the Gautschi type, with or without sloping melting hearths, and other designs; and to what extent duplex processes such as are used so much in Germany are necessary or advisable.

I know that they will answer that it depends whether you want to make rolling slabs or castings, but I think that it would be of great value to get an expression of opinion as to the best methods of melting aluminium for different purposes, because as we go through Germany and France and Scandinavia we see a great variety of different furnaces. There is no doubt that each has its merits, but I should like to have an opinion on what is the best melting equipment, especially when dealing with rolling mill slabs, first when dealing with

virgin metal and secondly when dealing with various forms of rolling mill and mixed scrap, and also for the remelting of foil, which is a problem in itself.

The amount of scrap made in aluminium works has been mentioned by Messrs. Thomas and Fowler, and I think that this gives great scope for the improvement of technique and equipment. It is a challenge, undoubtedly, to engineers and metallurgists who are designing equipment and furnaces, to solve these different problems in the aluminium industry which have been brought to focus in these two papers in an unprecedented way in technical discussions.

With regard to the heat-treatment of aluminium strip, I think that one promising method has been neglected, and that is induction heating. To my mind, some of the catenary and vertical strip furnaces which are being built in the U.S.A. for the steel trade are rather a nightmare, and it may not be long before the heat-treatment of strip will be done by induction in a very small space, as only a few inches of metal at a time need be heated for the heat-treatment of certain qualities of aluminium.

It would be interesting to hear any remarks that MM. Matter and Lamourdedieu care to make on the subject of what they expect to do in France with induction heating, because I believe that there is a great future in that direction, and in England we are working experimentally along those lines. I thank the authors very much for their informative and challenging papers, which I am sure will do a great deal of good in throwing light on the vast subject of the working of aluminium.

DR. F. W. HAYWOOD,* B.Sc. (Member) : As a British furnace manufacturer who has had some experience of non-ferrous heat-treatment, I have read these papers with particular interest. The latter part of the second paper, dealing with heat-treatment and flash annealing in particular, calls for comment, and I shall attempt to show that furnace manufacturers are alive to the problems raised, and that, given the necessary close collaboration with the producers of aluminium strip, the problems connected with continuous flash annealing will be solved.

The authors state that, with regard to the form of heating which should be applied, existing and well-tried methods would be available. Briefly, these methods are as follows : (1) Induction heating; (2) salt baths; (3) direct contact heating for example, passing over a heated drum; and (4) high-speed air-circulation convection heating. It is not proposed to discuss these methods in detail, but to confine my remarks to (1) and (4), namely those methods which appear to us to offer the most likely solution to the problems raised.

With regard to induction heating, the basic principle of heating a metal strip by induction produced by a transverse alternating magnetic field has been applied in industry to many problems. We have carried out preliminary work from both the theoretical and practical angles on the application of low-frequency induction heating to aluminium strip. Our work has shown that the heating of the strip to annealing temperatures can be accomplished with reasonable efficiency of power to heat transferred, and at a rate of heating sufficient to reach the required temperature in a few seconds, provided, of course, that the initial power input is sufficiently high to provide the heat equivalent required by the basic thermal laws.

The strip to be flash-annealed passes between coiling and uncoiling rollers, the unsupported strip between the rollers constituting the furnace—that is, a bank of inductors. This consists of a number of pairs of vertical iron-cored inductors, each pair comprising an upper and lower member separated by a gap of variable width, through which the strip passes. This gap is variable

* Technical Director, Wild-Barfield Electric Furnaces, Ltd., Watford.

separately for each pair of inductors from zero to a maximum of 2 in. This initial gap adjustment is provided to enable uniform heating across the strip to be achieved.

When the inductors are energized, alternating magnetic flux passes across the gap, inducing eddy currents in the strip, which thereby becomes hot. The temperature obtained is controlled by the speed at which the strip is coiled, or by automatic voltage regulation. Our experimental work indicated that strip 18 in. wide by 0.036 in. thick could be raised to annealing temperatures at the rate of 30 ft./min. with a power input not exceeding 130 kW. Furthermore, there appears to be no sensible upper limit to the width of strip which can be processed.

The difficulties associated with this method are concerned more with the continuous strip and its manipulation than with the induction heating. For example, lateral wandering of the strip would cause uneven heating, and there can be no assurance that the strip would maintain a plane surface during its entire passage through the inductors, though it is possible that the reduced tension necessary at annealing temperatures will result in far greater variations, which will require some automatic electric compensating device. It is our considered opinion that a considerable amount of research work into the high-speed coiling of strip together with the permissible tension at annealing temperature, will be necessary before a large-scale plant can be produced. This, as the authors rightly point out, asks for the closest co-operation between the furnace builders and aluminium fabricators.

Turning to high-speed air-circulation convection heating, this method undoubtedly provides a rapid heating of strip material. One of the first problems put up to furnace manufacturers was the flash annealing of metal in single flat sheet form, for example circles and sheets, and this has been accomplished (Fig. A, Plate CXXXV).

With regard to the authors' statement that there is at present no suitable equipment available for the flash annealing of the metal in coil form, we would say, from our experience of the heat-treatment of other materials in coils, that it is improbable that any simple method will be produced to give flash annealing in this form. We favour the strip being uncoiled and passed through a furnace for flash annealing, the strip being recoiled after annealing.

The various types of flash-annealing furnace suggested by the authors are as follows: (i) horizontal, (ii) catenary, and (iii) vertical. While catenary and vertical furnaces are common for the heat-treatment of continuous strip, other materials, such as mild steel, silicon irons, cupro-nickel and the like differ from aluminium and its alloys in that the heat-treatment temperatures normally employed are far removed from the melting range of these alloys and do not cause undue elongation at temperature. In certain cases, if surface imperfections arise these can be eradicated by a further cold pass.

From our work on the flash annealing of circles and sheets we believe that the flash annealing of continuous strip can best be carried out in horizontal-type furnaces, for the following reasons:

(1) The strip can, if necessary, be supported during the whole of its passage through the furnace. There are problems to be overcome, such as abrasion of the strip, synchronization of conveyor feeds with coiling and uncoiling gear, and retention of a plane surface, but all these problems are under investigation.

(2) There is less tendency for the strip to elongate at temperature. In short, we believe that no difficulty exists in supplying the necessary heat where it is required, but we agree that the mechanical equipment—comprising coiling and uncoiling gear, tensioning equipment, supporting rollers, welding or stitching machines, shears, &c., all built and controlled to ensure that the strip will not be damaged—presents difficulties. With collaboration between all the parties concerned, however, these difficulties can be overcome in the near future.

MR. C. E. DAVIES * (Member): As one of the oldest members of the Institute of Metals, and also as an engineer who has spent the best, or possibly the worst, part of his life in connection with the design and construction of rolling mills, a large proportion of which in recent years have been used for the rolling of light alloys, I want to say a few words to express my appreciation of the opportunity which we have had of reading two such excellent papers, of practical value to the industry and also to the mill designer.

As an engineer, I am naturally most interested, in the paper by MM. Matter and Lamourdedieu describing the new factory at Issoire, in the section dealing with the rolling plant, particularly as, by the courtesy of the authors, I had the pleasure of visiting the Issoire works earlier this year. This installation of wide strip-rolling mills for the production of sheets is, of course, based on modern practice, largely developed in America, and also generally in accordance with the latest developments in Great Britain. The main difference is that the roll-face width is greater than has as yet been called for in our country—2840 mm. as against, I believe, about 2200 mm. I presume that the plant is intended for the production of sheets probably not more than 2m. in width, and I wondered whether it was the opinion of those experienced in the production and use of rolling mills for wide strip that it is a good thing to have a roll face which is considerably wider than the maximum width of strip which it is desired to produce.

Referring to the hot reversing mill, I was interested to see that vertical edging rolls are provided. So far as I know, edge rolling has not been tried in Great Britain for aluminium and light alloys, although it is common practice with steel, and is used in at least one case for copper alloys. If edge rolling will eliminate, or at least reduce, edge cracking, considerable economy in manufacturing costs should be obtained. Have the authors any practical data on this, obtained as a result of experience?

A very interesting feature, on the electrical side of the installation, is the use of mercury-arc rectifiers instead of the more usual Ward-Leonard equipment. I had not heard before of rectifiers being used for such considerable powers as at Issoire. I have made inquiries of our electrical friends in England of the possible advantages to be obtained by a rectifier system, but on the whole they do not seem inclined to recommend it except for certain limited cases. Generally, I understand that for hot strip mills which may run at *set speeds*, like the tandem hot mill at Issoire, and others in England, and slow down under light load, there is no objection, and probably there is a considerable increase in efficiency as compared with the motor-generator equipment; the light-load losses should be less, and I understand that an 8–12% saving in consumption has been indicated. In the case of reversing mills the rectifier system has not yet been recommended or apparently developed to any great extent in England, and the equipment in such a case must be very complicated. For cold mills the conditions are not so favourable for rectifiers, as the acceleration has generally to be carried out under load, and there can be no doubt that there may be heavy peak demands. The experienced designers concerned with the electrical plant for the Issoire mills have no doubt dealt effectively with the difficulties suggested, and apart from these difficulties there appears to be a definite economic advantage in the rectifier system. It may now be developed to a greater extent, or at any rate studied to a greater extent, in England.

I notice that the weight of the housing differs in each unit, the heaviest being in the cold train. As the support roll diameter and face width is the same for all, I assume that the essential section of the housing posts is the same, and the difference in weight is due to some accessory equipment such as screw-down. I see no reference to the speed range of the cold tandem mill. Is the speed more than the speed of the hot tandem train?

* Director, W. H. A. Robertson and Co., Ltd., Bedford.

The paper by Thomas and Fowler is aptly complementary to the other one, and especially valuable in setting forth technical problems in the production of aluminium and light alloy strip and sheet, not directly connected with mechanical plant employed, but of the greatest importance to all concerned with the rolling processes. We are greatly indebted to the authors for giving such a complete summary of their study of these problems, and invoking the aid of the engineers and chemists and oil specialists to help to solve them. It is not only the rolling mill which does the job, but something else as well; as the authors point out, the choice of suitable lubricant for the cold rolling of aluminium and its alloys is of the highest importance. All of us concerned with the design and operation of plant for this purpose, and for rolling any metal in high-speed mills, have realized this for some time past.

In the case of the rolling of aluminium and its alloys the problem is difficult because of the conflicting requirements and the need for a lubricant which will fulfil the conditions in the rolls themselves and at the same time give the quality of surface finish demanded. I have always felt that research work on metal rolling has not always given the question of roll coolant and lubricant the attention it deserves, and we need help from the people concerned in operating the plant. The problem stated by the authors is most difficult with cold rolling, and especially when finishing lighter gauges, an extreme case being aluminium foil, which is rolled in England at 350 m./min., and new mills are being installed for higher speeds. In the case of aluminium foil rolling, the problem has to some extent been met by the use of suitably blended oils and controlled distribution. Moreover, by varying the coolant lubrication over a series of reductions or passes it is possible to finish with a light and easily volatilized oil and avoid the production of stains before or after final annealing. It may not be practicable to follow this practice in sheet and strip rolling. It should not, however, be impossible for the chemists and oil specialists, with the help of people like the authors, to solve the problem.

Another problem which is most interesting is edge cracking and "crocodiling". These troubles are most serious with certain alloys. As mentioned earlier in reference to the first paper, edge rolling at the stage at which it is introduced should reduce, if not eliminate, edge cracking. There is an inherent tendency for edge cracking to occur in any rolling process, inasmuch as the lateral spread of the metal is concentrated at the edges, with the result that the elongation of the edges does not keep pace with that at the centre, and so a tension is caused which is cumulative, and cracks are developed. If there is inherent weakness in the metal this tendency is exaggerated, and the harder the metal the more serious is the edge cracking.

The authors mention that the provision of edging rolls would involve heavy additional capital expense. This depends on the power of the unit which is required and the maximum thickness to which the edging unit is applied; it should not be a serious proportion of the total cost of mills of the size which we are considering. If some saving in scrap losses due to edge cracking could be obtained, the extra expenditure might be justified. The authors suggest that increased convexity of the edges of the slab would help. I thought that at first, but it might exaggerate the unequal elongation.

The authors also mention that if the shaped edge is presented to the rolls it will reduce the risk of "crocodiling". I can see this in widening or cross rolling, but if the slab is rolled in both direction the ends of the ingot as well as the edges must be rounded or bevelled. Would it be practicable to scalp the ends of the ingot to give a bevelled edge? Scalping is not a popular process with rolling-mill operators, but would it be an advantage to scalp the round cast edges?

The authors have also referred to temper-rolling, making small reductions of 10% or less after annealing. It is very uneconomical and difficult to effect

such light passes on heavy four-high mills, and I suggest that heavy two-high mills specially designed and arranged to take single passes might fulfil this purpose. A very useful mill for metre-wide strip with hydraulic roll-pressure control has been developed, and a similar design with larger rolls for double the width is quite practicable.

MR. W. C. F. HESSENBERG,* M.A. (Member): I have read both these papers with considerable interest, but I propose to confine my remarks to the question of cracking, referred to in the paper by Thomas and Fowler. The authors have adopted the usual practice of tending to throw the blame on the metal, and I want to emphasize, in fairness to these alloys, that the rolling process itself is quite conducive to cracking, even in the best circumstances. The reason for this is that tensile stresses are developed along the surface and along the edges of the ingot during rolling.

The surface stresses have been studied thoroughly in America, by Baker, Ricksecker, and Baldwin,† who have shown that longitudinal residual stresses are left in the ingot after it comes through the rolls. If the centre of the ingot is weak, the two halves tend to bend up, and crocodiling occurs. If the metal is generally sound, but somewhat tender, the surface gives way and transverse cracks appear at right angles to the direction of the principal tensile stresses. Baker and his co-workers studied this effect for different roll sizes and different thicknesses of ingot, and they found that the tendency to crack was reduced by keeping the ingot as thin as possible in relation to the size of the rolls, or the rolls as large as possible in relation to the thickness of the ingot. I know that there are practical difficulties in reducing the size of the ingot or increasing the diameter of the rolls, but here is some indication of an amelioration of the trouble. The remedy is to use as large a roll as possible, and as thin an ingot.

The tensile stresses at the edge of the strip are not so well understood, but I should like to show you some interesting results which we have recently obtained in the B.I.S.R.A. Metal Flow Laboratories, which have a bearing on the authors' remarks on edging:

1.3% carbon steel	(R) * 23% reduction before cracking.
	(S) 61% " " "
1.5% tungsten steel	(R) 10% " " "
	(S) 53% " " "
Aluminium-7% magnesium alloy	(R) 48% " " "
	(S) 60% " " "

* (R) = round edges. (S) = square edges.

These are three alloys which are rather difficult to roll and which are prone to give pronounced edge cracking. They were prepared in the form of cold-rolled strip, and in the soft condition. The edges of these strips, before they were rolled, had been surface-ground round or square in each case, so that one sample had round and one had square edges. The figures given are for the percentage reduction at which cracking first appeared on rolling. With round edges, with the 1.3% carbon steel, you can roll to 23% before cracks appear, and with square edges to 61%. With the tungsten steel you get only 10% with round edges, but 53% with square. With the aluminium-7% magnesium alloy you get to 48% with round edges, but there is an appreciable improvement if you square the edges up.

This shows that in edging of ingots it is not just a question of consolidating

* Head of the Mechanical Working Division, British Iron and Steel Research Association, London.

† R. McC. Baker, R. E. Ricksecker, and W. H. Baldwin, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1948, 175, 337.

the cast structure but it is important to get the edges straight, and the results claimed by the Americans in using edge rolls are based as much on the mechanics of the rolling process as on the metallurgy of the ingot.

I want to emphasize that in looking for a remedy to these problems we must keep our eye on what happens between the rolls as well as on the metallurgy of the ingot itself.

MR. W. H. BOWMAN * (Member): I should like to congratulate Mr. Thomas and Mr. Fowler on producing a paper which embraces in simple language the whole field of aluminium fabrication from the ingot to the finished sheet or strip.

I believe that a paper of this calibre should be considered as a text-book for young engineers, metallurgists, and physicists who are entering the industry from the universities, as I am sure it will introduce them to some of the pitfalls and problems to be met and to be solved in the aluminium industry. There is no doubt that the authors have raised in no uncertain terms some of the problems now being met with in practice in both the foundries and rolling mills of mass-production units.

Referring to the foundry, it is recognized that semi-continuous casting has shown considerable advantage over the older methods, but it has also brought with it its own difficulties, and these can be solved only by careful study; but I should like confirmation from the authors as to whether they have experienced any reduction in the casting cost per unit of metal compared with that of the permanent mould. My own experience is that the advantage of continuous casting over the permanent mould is metallurgically better castings of much larger sections and weights than could be produced with the permanent mould, but there has been no material reduction in any production costs. Is this the authors' own experience?

It is also my experience that the high-strength alloys have to be cast in smaller sections than the pure and near-pure alloys, and we have effected some improvement by minute adjustments in the specifications of these alloys and have found that very careful and accurate temperature control of the water for chilling, together with uniform and constant application, does result in a reduction of cracking, but there are still other technical snags not yet "pin-pointed". It has also been our experience that when casting high-strength alloys, cracking can be reduced to a certain extent by not using the virgin mix, but by introducing a certain amount of process metal, though at this early stage I cannot give any reliable percentages.

My own company is installing large continuous-casting units, and arrangements are being made for increased quantities of close-temperature-controlled and filtered water application. The equipment is so designed as to give pouring speeds up to 15 in./min., as we are of the opinion that the faster the near-pure alloys are cast, the less scalping, if any, will be required. The problem of increasing the speeds of the high-strength alloys is not so simple, but again careful study of the difficulties should help to make this possible.

I think that the authors are correct in emphasizing that the cost of scalping and remelting swarf, with the resultant metal losses, can be as high as half the total cost of casting, and it is with this in mind that the industry should spare no pains in tackling this most important problem of the reductions of scalping.

In regard to the rejections for blister, I should like to ask the authors whether a satisfactory method has been found for introducing degassers into a large holding bath of, say, 10,000–15,000 lb., which is the order of capacity in modern furnaces feeding continuous-casting units. We intend to introduce degassers at the four corners of the holding chamber.

* Executive Director, T.I. Aluminium, Ltd., Birmingham.



FIG. A.—Electric Furnace for Flash Annealing Aluminium Circles.

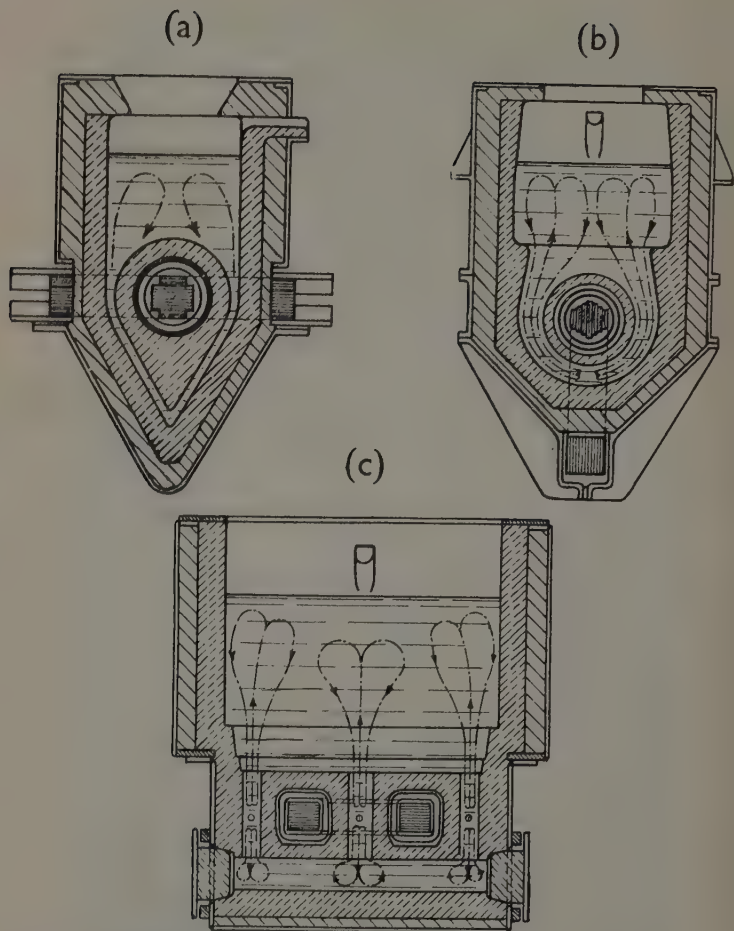


FIG. B.—Development of Low-Frequency Induction Furnaces. (a) Copper furnace. (b) Old-type aluminium furnace. (c) New-type (Ajax-Tmma) aluminium furnace.

The handling of process scrap is one of the problems of modern aluminium strip-mill practice, and I feel that one way of solving this problem is by having a massive baling press with sufficient capacity to take care of sheets and strip up to $\frac{1}{8}$ in. thick, which is the usual thickness of stock from modern hot mills, and compressing it into blocks, and in this form it is more conveniently stacked and subsequently handled in the remelt furnaces. A baler of this type would eliminate a tremendous amount of cutting up necessary when introducing the material from scrap boxes straight into the furnace, and one can almost consider it a form of ingot, which is the most desirable form of material for charging into a furnace.

On reading Section V, "Scrap Remelting", I assume that it is the authors' view that the furnace for receiving the 10 cwt. of scrap is the orthodox duplex melting and holding type of furnace, and I should like to have their confirmation that this is the case.

I must admit that there is still the problem of the large scrap coil, but perhaps the solution is to shear it up on the ordinary Hallden processing line, and then bale it with other process scrap.

Referring to the hot rolling of strong alloys, I do think it has been proved that the introduction of edge rollers in front of the hot mill has materially reduced edge cracking, but, as the authors say, it is a very expensive piece of plant, and so far no one in this country has gone to that expense; but according to the paper by MM. Matter and Lamourdedieu such a unit has been installed in the aluminium plant at Issoire, and I am looking forward to seeing this.

It is my experience that the soluble oil on hot-rolling mills should have its temperature very carefully controlled and should be filtered to an extent of 10-15% of the total throughput, preferably with fuller's earth filters, so as to make sure that no oxide or foreign matter is rolled into the surface of the hot-rolled blank. If this is carried out effectively, it is possible to roll to much thinner gauges in the hot stage and still finish with a clean product.

We have found by bitter experience that it is essential to have soft water in making up the soluble-oil solution; otherwise the result from the hot mill is strip with a cloudy appearance, and this defect is not removed by subsequent cold-rolling operations; and incidentally, this same effect is caused in the heat-treatment process when hard water is used in the quenching tank.

In respect of cold reduction, my own company has given very careful thought and consideration to the lubricant required for the cold rolling of aluminium in strip form at speeds up to 1000 and 1200 ft./min., and there is no doubt it will be necessary to instal pressure flood lubrication with a light mineral oil incorporating certain additives, and that this will have to be filtered and cooled as it is collected from the rolls. In this instance we are relying on the very close co-operation of the oil industry to supply a product which will stand up to this very severe punishment, and at the same time carry out its main function of dissipating the heat produced by rolling and avoid staining in the annealing process.

I think that the question of annealing and heat-treatment in continuous strip form could be considered by the furnace designers as one problem, and I understand some studies have already been made with this type of furnace by British furnace builders.

One thing that concerns the practical people in continuous strip annealing and heat-treatment is the floor space taken up by these units. We ourselves already have had certain experiences with a 4-ft. single sheet annealing furnace, and have found that owing to the variation in the width of the product, and especially where we are annealing circles, our heating and labour costs are much in excess of those with the orthodox type of annealing furnace, although it is agreed that the resultant product is very much improved. It is essential

that these points be considered and a satisfactory solution found if the industry is to change over its form of annealing and heat-treatment.

As an engineer, I feel that some of the annealing problems may be simplified by a modification of the alloy in order to give the same strength in the annealed condition as was previously obtained in the $\frac{1}{2}$ - or $\frac{3}{4}$ -hard condition. For instance, much trouble is experienced in producing $1\frac{1}{4}\%$ manganese alloy in $\frac{1}{2}$ - and $\frac{3}{4}$ -hard conditions, such as may be required in the box-making industry, and I believe steps are already being taken along this path for box material. If this should be successful, it may open up the field for supplying the modified alloy in the annealed condition in sheet form, so affecting the problem of annealing particular alloys in coil form with subsequent grain growth, &c.

I believe, therefore, that consideration should be given to approaching the problem by modifying the alloy before we become involved in complicated designs of continuous strip annealing, as unless we can simplify the methods of production, we shall never operate these large production plants in their most efficient manner.

I think that the authors in their conclusions have stated the main problems to be solved, either by the engineer, by the metallurgist, or by the physicist, or a combination of the three of them, before we are in a position to operate modern strip mill plant at its highest efficiency, but I would say that all these problems could be solved much more quickly if the industry as a whole would energetically compare their experiences. Surely this would mean a quicker answer and, therefore, a cheapening of costs and a broadening of the demand for aluminium, which is the aim of all progressive people in the industry.

PROFESSOR DR.-ING. A. VON ZEERLEDER* (Honorary Corresponding Member to the Council for Switzerland): I should like to congratulate my friends MM. Matter and Lamourdedieu on their very interesting paper. It gives a great deal of new information which we have never had before in any publication. I received the paper only last week, being myself engaged at another international meeting, and so I have not been able to study it in detail. I shall therefore confine myself to giving the experience of my company, the Swiss Aluminium Company, on one problem which has been discussed, namely the melting problem.

In the last sixty years we have used almost all types of melting furnace—coke-fired, oil-fired, gas-fired, electric arc, resistance, and low- and high-frequency furnaces. I think, however, that the most interesting problem is provided by the results of the induction furnace. This induction furnace, I see from the paper, is installed at Issoire, and it will be of great interest to us to compare the results with the oil-fired furnaces used there. The problem of melting aluminium is a very intriguing one, however, and it is not a question of there being only one answer or of one furnace being right for every purpose.

We have first to face the most interesting problem caused by gas. I think that the aluminium industry throughout the world loses millions of pounds every year owing to gas troubles in sheets, forgings, extrusions, and so on of aluminium, and I think that half the troubles that occur in rolling aluminium and its alloys are due to the melting processes employed. You may say that the trouble arises from the metal that is melted, but by bad melting you can spoil even a good metal, and by appropriate melting a bad metal can be very much improved, so that the greatest importance must be attached to the melting process.

Then there is the oxidation loss, which is more a commercial matter. The condition in which the metal comes to the foundry is of great importance, and so is the type of scrap; lastly there is the use of the metal—whether you have

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rolling mills producing only one or two alloys in very big lots or whether you have a mill which has to produce half a dozen or a dozen different alloys, sometimes only in small lots. All this will have an influence on the decision as to which type of furnace to instal.

We ourselves started with low-frequency induction furnaces in 1937, and it was with Mr. Tama that I constructed the first aluminium induction furnace used outside Germany. Germany was a year ahead of us. Mr. Tama was a very famous man in the brass industry, and introduced the Ajax induction furnaces in the German brass industry. He was a specialist on induction furnaces, and is now a Vice-President of the Ajax Company in America and probably the best man for the construction of induction furnaces for aluminium.

Our first furnace was a 125-kW. furnace, and we then raised the capacity to 250 kW. To supply a big demand for molten metal, we therefore need a battery of such furnaces. To meet this demand, Tama developed 500-kW. and even bigger furnaces up to 1000 kW. This larger type has the advantage of a greater output, and also a better efficiency and lower cost of labour.

The greatest trouble with the induction furnace is the necessity for cleaning the loop. You probably all know the principle of the induction furnace (Fig. B, Plate CXXXVI). You have the loop which forms the secondary, and inside you have the transformer with its primary winding and its iron magnetic core. With brass there is no deposit in this loop, and it keeps clean and there is no trouble with cleaning it; but with aluminium there is the disadvantage that aluminium oxide is deposited in the loop, and after the furnace has been running for six or eight hours the loop begins to fill, and the material acts as an electrical insulator and no current goes through it. The furnace will break down if you do not clean the loop, and it is a very disagreeable operation; you have to remove the metal from the furnace and with an ingenious cleaning chain clean the loop, and this has to be done, as I have said, normally every eight hours.

Tama made a very important improvement by building this loop with a plug at one side for cleaning. This makes it possible to do the cleaning operation without taking the metal out of the furnace, by a tool which is introduced, and every eight hours you have only to pass this tool two or three times through the two vertical channels to clean them. You do not need to clean the horizontal channels. Normally once every month the furnace is emptied, the plug taken out and some dross which may have collected there is removed; but one of the service engineers from the Ajax-Tama Company told me that they have furnaces which have not been stopped for more than a year, and they have only cleaned the vertical channels. This trouble, therefore, no longer exists, and that is a very important improvement.

The first problem to which I referred was that due to gas. With this type of furnace the metal is thrown out of the loop and comes in again, and so the metal is in constant circulation. We thought that this circulation would give rise to a greater gas content in the metal than with the other type of furnace, where the metal is quiet and not in constant movement. We find, however, that metal melted in these induction furnaces has no more gas than metal melted in any other type of furnace; on the contrary, the degassing effect is better. Moreover, we have a cold atmosphere on the top of the metal, and the atmosphere is much colder than the metal. With every other type of furnace, using combustion or electrical-resistance heating, the heat always comes inwards from the surface, so that the atmosphere is hotter than the metal, and therefore there is more tendency for the metal to take up gases out of the atmosphere than in the induction furnace. The loss, by oxidation, is definitely smallest in the induction furnace, for the same reason, and compared with resistance furnaces there is the advantage that you can use fluxes in the induction furnace which you cannot use in the resistance furnace, because the gas developed by the flux would immediately spoil the resistors.

In my opinion big induction furnaces of 5–10 tons capacity are from the metallurgical standpoint the best melting furnaces for aluminium, especially for thin scrap. The melting loss is much smaller than with other furnaces. Table A* gives a comparison of coke-fired, electrical resistance, and induction

TABLE A.—*Operating Costs for Melting One Ton of Metal in Different Melting Furnaces (Approx.).*

COKE-FIRED OPEN-HEARTH FURNACE.		<i>s.</i>	<i>d.</i>
Loss of metal as dross 42 lb. at 8-8d., say		30	10
Coke consumed 391 lb. at 65s. per ton, say		11	5
Wages 12 man-hours at 2s. 2d., say		26	0
Repairs (material and wages)		7	0
		<hr/>	
		75	3

CARBON-RESISTOR (CHANNEL) FURNACE.		<i>s.</i>	<i>d.</i>
Loss as dross 24 lb.		17	7
Power 550 kWh. at 0-7d., say		32	1
Gas carbon 9 lb. at 1d.			9
Wages 2 men, 550 lb. per hr.—8 man-hours per ton		17	4
Repairs		3	6
		<hr/>	
		71	3

NICHROME RESISTANCE FURNACE.		<i>s.</i>	<i>d.</i>
Loss as dross 24 lb.		17	7
Power 450 kWh.		26	3
Wages 2 men, 550 lb. per hr.—8 man-hours per ton		17	4
Repairs (heating elements, shielding plates, &c.)		4	0
		<hr/>	
		65	2

INDUCTION FURNACE.		<i>s.</i>	<i>d.</i>
Loss as dross 18 lb.		13	3
Power 430 kWh.		25	1
Wages 3 men, 600 lb. per hr.—11 man-hours per ton		23	1
Repairs		1	6
		<hr/>	
		62	11

furnaces. Of course the price of fuel and electricity has a big influence on the economy of the melting process.

MR. B. N. H. THORNELY †: MM. Matter and Lamouredieu have given us a remarkable story of vision in planning the Isoire works before the war and of determination in carrying out the project in spite of almost insuperable difficulties. It may be of interest to mention that the first mill, which was tossing about on the Atlantic when the armistice came in 1940, found its way to our works at Rogerstone in Monmouthshire. We used it as a hot reversing

* For fuller details see my "Technology of Light Metals", 1949 (Elsevier Publishing Co.).

† Chief Engineer, Northern Aluminium Co., Ltd., Banbury, Oxon.

mill, and it enabled us to increase the weight of our coils considerably and to improve our strong-alloy production very much indeed. That mill has been working there ever since.

It is said that the mill at Issoire was conceived with the idea of catering for the motor-car market. That, of course, is a market which we all have our eye on, and it would be interesting to know what the reaction of the motor-car industry is when the material is available, and what other markets for large tonnages of sheet seem to be available in France.

Only heat-treatable alloys are mentioned, I think, in this paper. It would be interesting to know whether the production is to be confined to these alloys or whether they will also roll work-hardening alloys.

In the description of the hot line it is said to be possible to take the slab off the line for reheating when necessary. I should be interested to know when it is considered necessary to interrupt the rolling and to reheat and when one can roll straight down in one operation.

The section mills, I understand, have not been installed, but it was planned to roll sections rather than, as we do in England, to extrude them. There seems to be a good deal to be said for both methods of production. If you extrude sections you have a wider variety of shapes and are better able to cater for prototype production in the aircraft industry, but if you roll, as long as you have a reasonably small number of sections, I imagine that you can produce more cheaply. It would be interesting to know what determined the authors' choice.

The paper by Thomas and Fowler is a most interesting and useful analysis of the problems which are common to all companies turning over from old methods of production to new, high-speed rolling. This seems to be a very opportune time to bring these problems out into the open and discuss what has been done to solve them. Taking first of all the question of scrap melting, the fundamental objects to keep in mind are low melting losses; high-speed melting, so that you can reduce your labour cost; and low handling cost of the scrap from the time it is made to the time it is melted. The fundamental drawback to reverberatory furnaces is that all the heat passes into the metal through the surface of the molten metal, which is very highly reflective, and that surface must be kept at the highest possible temperature consistent with metallurgical considerations if you are going to get heat quickly into the solid metal underneath.

This problem was set out very clearly at a recent Iron and Steel Institute meeting, and it was proved, at least on a small scale, that the most economic way of melting was to melt on a ledge, so that the solid metal is directly underneath the hot roof of the furnace, and let it melt there and trickle into a holding bath in the centre. In the case of aluminium I imagine that that would involve too high a melting loss. The alternative suggested in the paper, of a preheating hearth where you at least get some heat into the solid metal and drive off the oil before you put it into the molten metal, is still going to mean rather a slow furnace, because all the metal has to be melted in roughly the same part of the furnace, that is to say at the end of the hearth.

I wonder whether we shall not all be using induction furnaces for this job soon, because there, as has already been said, the heat is generated underneath the bath and the surface itself is at the minimum temperature; the whole charge can be melted in a semi-liquid state, so that you do not raise the temperature unnecessarily at any stage, and the heat is generated in a very small space, which makes the charging of scrap a much easier problem. The furnaces are also of a type which can be located outside the normal melting shop, and they do not create a lot of heat round them. It should be possible perhaps, to locate them at the source of the scrap, as is evidently done at Issoire, where they have the induction furnace in the metal store.

Turning to edge cracking and crocodiling, the influence of a small percentage of impurities has been mentioned, and I should like to confirm that. During the war, we had a serious epidemic which was eventually traced to the presence of 0.02% lead. This lead had got in from melting up wrecked aircraft, and it gave us a great deal of trouble. Another question, which has not been mentioned, is contamination from the furnace lining. That is a serious problem, particularly where you change from one alloy to another very frequently; and it is also serious when you melt magnesium-zinc alloys, in which the silicon content must be kept low to ensure good casting characteristics. Our feeling is that the most serious cause of edge cracking and crocodiling is inefficient or inadequate preheating, and in my view the period of 18-24 hr. mentioned by MM. Matter and Lamourdedieu is more suitable than the 12 hr. mentioned in the second paper. I also wonder whether a four-high breakdown mill would not have a good effect on crocodiling, owing to the fact that the smaller work rolls would tend to work the centre of the ingot more thoroughly than a larger roll.

This paper by Thomas and Fowler very well illustrates the modern technique and the interaction between the research laboratory, the engineer and plant manufacturer, and the works staff. For modern high-speed production it is essential that all those people should be brought into the solution of problems. I think that it is true to say that in a works which has solved those problems a more stable and standardized practice is evolved and the products are more uniform than they were from the older type of mill. They have more uniform grain-size, better gauge control, better flatness, and more uniform surface finish. I think there is no doubt that the product of these mills is of a type which is more suitable for use in the mass-production industries, where it is hoped that we shall sell large quantities of sheet.

MR. CHRISTOPHER SMITH * (Member): I have very much enjoyed reading both these papers, but my remarks will be directed mainly to that by Messrs. Thomas and Fowler. This is an eminently practical paper, in that it poses the problems which are of greatest concern to the industry at the present difficult period.

I should like first of all to make a few observations on a number of the points raised in the paper in the hope that they may promote in others some germ of thought. It is always interesting and sometimes instructive to hear others discussing our individual problems.

The difficulty arising from bleb formation on the strong alloys has always been with us. I have seen no really successful approach to this particular problem. A process was devised in Germany during the war in which the mould was vibrated by an out-of-balance motor during casting. This resulted in a more even distribution of the exudation rather than in a reduction in its amount, but clad sheet was being successfully produced from the resultant slabs without machining them before covering. I should not care to vouch, however, for the corrosion-resistance of the finished sheet.

It is clear that the exudations develop in the air gap between the billet and the mould wall, and their development may be observed by studying those surfaces of cast blocks which remain within the mould. There is one method of casting which appears almost completely to prevent the development of blebs, and that is the method in which a very thin-walled mould, shaped rather like a bucket (i.e. tapered upwards), is filled with liquid metal and lowered slowly into cold water in order to induce directional solidification. As solidification commences the billet settles down slowly in the mould so that there is never an air gap between the wall of the billet and that of the mould. The amount

* Chief Metallurgist, James Booth and Co., Ltd., Birmingham.

of taper is, of course, critical. This suggests that the application of ingenuity to the semi-continuous casting process might offer some promise of considerably reducing bleb formation. It is appreciated that with cylindrical billets this might be difficult, since a mould which is tapered adequately does not permit the billet to pass through, but with rectangular shapes it might be possible to devise a mould using thin endless bands of metal foil which could be movable with respect to the billet surface and which could be spring-loaded to follow the contraction of the billet. Alternatively, some application of hydrostatic pressure might serve the dual purpose of compression and cooling. An interesting development somewhat related to this line of thought was that of the Eriical mould, which applied a similar technique but for a different purpose. Devices of the fanciful kind indicated above would if successful also markedly increase the efficiency of heat extraction, but might introduce further complications due to stress-cracking.

The authors' observations on blister will strike a sympathetic chord in most of our minds. Why do we get epidemics of blister? Years ago we were weak enough to blame the Clerk of the Weather, but I think in our hearts we were far from convinced. I am still of opinion that the great variation which we experience in the efficiency of degassing operations arises because of the great variability of these operations as practised in our own works. A long experience of the Hanson-Slater process convinced me that when properly applied it was entirely efficient. The difficulty lies in fulfilling all the requirements for efficient degassing. I feel that the way in which we most frequently fail in the degassing operation is that we do not provide a completely moisture-free atmosphere over the melt. The amount of hydrogen in the melt is a function of the amount of hydrogen on the surface of the melt, no matter what degassing agents we use. What the authors call "settling time" is also an important part of the operation of degassing, for undoubtedly melts which stand quietly for five or ten minutes continue to lose gas, provided correct conditions are maintained above the melt.

I should value expressions of opinion on the relative merits of different degassing agents. My own impression is that nitrogen or chlorine, or both together, give the most satisfactory results. I was interested to read that fluxes were not considered suitable for use with strong alloys. I am not sure that they are suitable for use with any aluminium alloys; they almost inevitably contain sodium and alkaline earth elements, and I believe some of these to be very harmful, especially in the presence of magnesium. Fluxes are also excellent purveyors of moisture. I should like to know more about the reasons why sodium is harmful in the presence of magnesium. It seems to me that there is more in it than just affinity for moisture during the various heating operations which arise in production.

Reference is made in Section V to precautions which might be taken to avoid gas pick-up in melting. Assuming that two melts, one of high and one of low gas content are properly degassed, would one normally expect them to vary in gas content after degassing? Is there any justification for taking the attitude that provided one has efficient degassing methods then costly precautions in melting technique are unnecessary?

Everyone has experienced the variability of behaviour of different batches of the strong alloys (and indeed of other alloys) in respect of the hot-rolling operation. May this in part be due to the presence of minute quantities of elements which are not normally estimated? I have in mind those elements of the sodium type which certainly affect disastrously the hot-rolling properties of the aluminium-magnesium alloys. Does virgin aluminium ingot vary in respect of its content of such elements, and is it possible that differences in virgin metal may affect the characteristics of some of our alloys in hot rolling? It would be nice to know that the producer of aluminium, like the Clerk of the

Weather, could be acquitted of this charge. I should also like to ask the authors if they have observed, with some casts which have crocodiled badly, whether keeping the blocks for a month or two has resulted in any improvement in rolling behaviour.

One final word on blister. Do the authors think that the amount of blister which occurs on clad material can be traced in part to the practice of rotary milling? I have occasionally seen blisters on arcs of circles in clad sheet and have thought that if the open ends of the machined arcs face the roll during cladding there may be a danger of air entrapment. The quality of the machined surface is also of importance.

The authors' observations on problems arising from the later processes of sheet manufacture are a real challenge to all light alloy technologists. There is obviously a very large scope for informed work on lubrication and cooling of rolls, and heat-treatment certainly seems to be the Cinderella of our processes. One would like to know more about the large-scale processes which were practised in the United States during the war, in which atomized water in the form of "fog" was apparently used successfully and resulted in a marked decrease in distortion. In this connection it is of interest to refer to the excellent paper on the new plant at Issoire. I note the details of the heat-treatment furnace used for extrusions, in which bars of apparently considerable size are quenched by atomized water sprays. Can the authors of this paper inform us whether bars of large diameter may be effectively quenched in atomized water? Are the properties in the core of large bars satisfactory?

The paper by Thomas and Fowler is excellently summarized in Section XII, and I should like to draw attention particularly to the emphasis which the authors put on the need for team work between the scientists and the production staff. I should like to go further and suggest that this team work must be carried to very great lengths. I feel very strongly that the research worker must not remain aloof from the shop floor. I think there is a danger that research workers may adopt what I can perhaps call an attitude of armchair criticism which will tend to inhibit development if they do not actually see for themselves the nature of the problems in actual process. There is a tendency in our modern methods of organization to isolate the research worker, and I think that there is a very real danger in this attitude. Very frequently there are aspects which arise in actual shop processes which escape the notice of the production engineer and works metallurgist, but which would inspire the mind of the informed research worker with ideas which would not otherwise occur to him.

MR. N. P. TAYLOR *: It is a pleasure to bring to the authors of these two very interesting papers our congratulations from Canada. I have read the papers with the greatest interest, and I feel that they form an outstanding contribution to the written matter that we have available. Messrs. Thomas and Fowler have certainly given the industry a most complete and thorough outline of the problems which now face it, and some good signposts to direct us along the way we ought to go to clear them up. This paper is most timely, because with the return to more easy supply of some of the other, competitive materials, the aluminium producers are going to have to resort to every device known to them to hold their gains and make the new ones for which they hope.

I think that the rather disappointing progress that we have made in solving some of our bugbears, such as that of gas in metals, and the fact that they are now beginning to yield to concentrated research, amply demonstrates the fact that the association of rather extensive and costly research organizations and the operating companies must be very close.

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We are engaging extensively in this type of work, and we are, of course, finding, in common with others, that it is very expensive. Research programmes cannot be carried out in a short time; they take a long time, and the number of people engaged on them is large. We therefore feel it will be necessary for the industry to engage in some "bread and butter" work to justify the cost of more research, and it is in this direction we are looking at present. It will be necessary to lay down expensive plant to pick up the so-called continuous, large-tonnage, single-purpose types of business, but we believe it will pay for itself and the associated research in the long run. At the same time we hope that many of the old problems which have dogged us for years on smaller operations will "come out in the wash".

With regard to the paper by MM. Matter and Lamourdedieu, I should like to compliment them on the excellence of their presentation and on the tenacity of purpose which has made it possible for them to bring this great plan to completion in spite of the difficulties which they had to face. The use of rectifiers in place of rotating Ward-Leonard equipment is also very interesting to us. We have talked about this on many occasions, and investigated it to some extent in America with the electrical companies there, but, perhaps owing to the fact that they were busy and able to sell all the rotating equipment which they could manufacture, they have shown little interest in developing rectifiers for mill drives. However, perhaps with the lessening of business they will take a greater interest in the matter.

Mention is made in this paper on the works at Issoire of dual heating systems on furnaces. I should be interested to know whether the method of applying oil firing to these furnaces is by means of muffles or radiant tubes, or whether the product of combustion is allowed to come in contact with the metal. We also have adopted this type of equipment in one or two cases in Canada.

M. J. MATTER (*in reply*): In considering the different remarks which have been made and the various questions put, it should be borne in mind that the works at Issoire is now an old works, because it was conceived and designed ten years ago. If it were being designed to-day certain alterations would be made. You must not be surprised, therefore, if you find certain things which correspond to the ideas of ten years ago. We hope to make various alterations in the course of the next few years.

Mr. Campbell referred to the electric remelting furnace. It must be borne in mind that comparisons between different countries are becoming more and more difficult because of the different conditions for the supply of electrical energy. In France conditions in this respect have undergone considerable change, and you must not be surprised to see oil being used in place of electricity. That does not mean that we find oil better, but by reason of the cost we may be obliged to abandon the electric furnace. That upsets the comparison of various types of furnace used in different countries.

M. M. LAMOURDEDIEU (*in reply*): Many of you will be going to Issoire, and it will be better to reply to some of the questions on the plant itself. On the question of the type of furnace to be used, the economic factor is very important, as the price of electricity is very high in France to-day.

The induction heat-treatment and annealing of coil is very interesting. We have had some tests going on and hope that in a few months' time it will be possible to give a better answer.

Reference has been made to the sale of aluminium sheet for automobiles. It is a little early to say much about this, because the plant is not working yet and we have had no contact with the automobile people, but it is hoped to develop this field of application.

Mr. Smith asked about the quenching of extruded bar. It is not possible at the moment to say anything very interesting about that, because the furnace is only just ready and not many tests have been made. We have seen the process used at many plants in America and it seems to be successful. That is the reason for applying it at Issoire, but we shall know more about it after a few months.

MR. W. A. FOWLER (*in reply*): To reply fully to all the comments and questions would take far more time than is at our disposal this morning. We shall, therefore, run briefly through the various questions in the order in which they were raised.

Dr. Haywood, dealing with the flash annealing of strip, referred to the two systems of induction heating and high-speed convection heating. We are aware that induction furnaces have been under consideration for a long time for the annealing of aluminium strip, but we are still waiting to hear the results of the experimental work which has been undertaken by various people who are interested. When we come to consider how the strip is to be held and controlled mechanically through the furnace, and the problems which may be associated with strip wander and strip distortion, we see that the problem is more difficult than may appear at first sight.

On the question of the horizontal furnace, which Dr. Haywood mentioned, we are very pleased to know that we are likely to get a furnace of the horizontal type which will do all the work we require of it, and without abrasion or damage to the metal. We look forward to hearing more from him in due course, once this furnace has been brought to completion.

Mr. Davies raised one or two interesting points. One concerned the roll face in relation to the sheet width. He was probably referring to the difficulties in this sheet-width-roll-face relationship on two-high mills. It was commonly accepted on two-high strip mills that a strip width of about 60-66% of the roll-face width was about the optimum width for successful results, and beyond this—say at 70-75%—the edge effect on the strip was such as to cause cracking and distortion, and not much success was achieved. With four-high mills, however, we think that the limits of this strip-width-roll-face ratio which apply to two-high mills are largely removed. It is common to-day to have a relationship of 75-80% in a four-high mill without any difficulty whatever.

Mr. Davies also referred to the question of lubricating oils, and drew some analogy between a small foil mill and a heavy modern high-speed strip mill. We think that lubrication in connection with a foil mill is a very different proposition from that of a heavy mill. The amount of heat generated, we imagine, is very much less in the case of a foil mill, and the cooling and associated problems are in consequence very much smaller.

Mr. Davies also asked why we did not wash the strip after rolling, to remove the oil. The point is that the washing is an additional operation, and the object with these modern strip mills of large capacity is to cut the number of operations down, not to increase them. We should much prefer to provide oil-free strip without the need to introduce further and expensive plant.

Mr. Davies mentioned the convex edges of slabs and the influence this has on edge cracking and crocodiling. When we spoke about the shape of the edges of slabs and its effect in inhibiting cracking, we should have made it clear that these shaped edges are offered to the rolls and maintained in that direction for as long as possible. If the size of the slab in relation to the stock which is being rolled is such that this direction can be maintained to a thickness of 2-3 in., there is no harm in then turning through 90° for completion of rolling. A considerable amount of work is imposed on the rounded edges of the strip during the first reductions, and that may be the explanation of why there is less edge cracking when the slab is turned through 90°.

Mr. Davies also asked whether it would be an advantage to scalp the edges. We think that it would be, but it is not a very simple or economical operation, and we tend to place our trust in the provision of edge-rolling mills, which we hear are doing very good work in America.

In a reference to temper-rolling, it was suggested that we should employ a heavy two-high mill to effect the small temper-reductions of, say, 10%. Our objection to these light passes of, say, 5-10% on such a mill is that it is probably capable of effecting reductions of up to 70%, and it is like putting a man on a boy's job. A more economical way of achieving the same results might be through the medium of "temper letting down".

We were very interested to hear of Mr. Hessenberg's work at B.I.S.R.A., and to know that the cracking of a slab is not necessarily associated with the metal itself or the casting of the metal, but can be associated with the types and methods of rolling. He said that the smaller the slab the less is the trouble experienced. We are dealing with something very large in these modern mills. From a slab of about 120-140 lb. in weight 20 years ago, and 400 lb. 10 years ago, we have now come to something of the order of 2 tons, without anything like a corresponding increase in roll diameters, and the technique of controlling cracking and fabricating must keep pace with the development of this size of slab. The small slabs which we had years ago would not be appropriate to the large mills in operation to-day.

Mr. Bowman asked whether we felt that any reduction in costs has been achieved by using the semi-continuous casting method as compared with the permanent-mould method. It does seem, from studies which we have made of the economics of the question, that there is a size of slab for which it is probably not profitable to change from an ordinary permanent chill-cast mould to the continuous system. We do not know whether a figure should be mentioned, but it is in the region of 400 lb. The reason why the semi-continuous method was introduced is that it is the only way to get the large slab to suit the modern mill. It is unfortunate that its development has been associated with other expenses—with the necessity, with strong alloys, and in fact with most of the alloys, to scalp to remove surface imperfections, and so on. That is why we emphasize in our paper that what we want to do is to get rid of the surface imperfections associated with the continuous-casting method, and when that is done the process will compare favourably with permanent-mould casting, almost irrespective of the size of the slab.

Dealing with scrap handling, Mr. Bowman suggested the provision of a massive baling machine. This might be satisfactory, but we want to dispose of scrap in bulk by the use of a furnace only, and thus avoid the purchase and use of any additional machines.

We were interested in the views of Mr. Thornely on edge cracking in relation to the effect of impurities generally, but it would be more appropriate to reply to these in writing.

Mr. Smith's views on blebs and the effect of mould vibration on blebbing were interesting. The only question which we can deal with at the moment, however, is in connection with the request for information on the best type of degasser. We feel that when we talk about the best degassers we have to have regard to the conditions in which they are used. We have known degassers which elsewhere have been reputed to be satisfactory give but indifferent results under the conditions operating in our own Works.

We should like, in conclusion, to thank you for the manner in which the paper has been received.

CORRESPONDENCE.

MR. W. A. BAKER,* B.Sc., F.I.M. (Member): Messrs. Thomas and Fowler cover many technical problems, and I shall confine my comments to a few points involved in melting and casting practice.

At two points in the paper, on pp. 928 and 931, the authors refer to the use of a slightly oxidizing or slightly reducing flame, the implication being that the associated variations in the composition of the furnace atmosphere gases might be expected to produce a marked effect on the rate of oxidation of the charge and/or on the extent to which the charge is gassed by contact with these gases. I find this difficult to believe because at the temperatures involved the reaction between aluminium and water vapour will proceed to completion, i.e. to the formation of hydrogen and metal oxide, irrespective of the concentrations of reducing gases like carbon monoxide or hydrogen in the atmosphere, and both oxides of carbon are reduced by aluminium. I should have thought that a more pertinent consideration was the velocity with which the furnace atmosphere gases impinged on the metal, and this is perhaps the factor which is controlled by adjusting the fuel: air ratio as suggested in the paper.

On pp. 927-929, the authors discuss the problem of dissolved gases and outline various methods used to degas these light alloys. They indicate that these methods are not entirely satisfactory, particularly with the alloys containing magnesium. It occurs to me that the trouble complained of may be due not so much to the ineffectiveness of the various degassing methods but rather to gas absorption occurring after degassing, including gas absorption occurring during solidification in the direct water-cooling process. The point is, that as the work of the B.N.F.M.R.A. has shown, light alloys containing magnesium even in amounts of the order of a few tenths of one per cent., are very prone to absorb hydrogen when they are brought in contact with steam, as for example when they are cast in sand moulds. It seems to me therefore, that the first step towards a solution of the problem is to obtain evidence on the condition of the metal at various stages in the process. In this connection, the reduced-pressure test used in our laboratories and described in my paper to the *Journal* † should be helpful, because by this means it should be possible to detect any increase in gas content during transfer of the metal from the furnace to the mould, and moreover when using the semi-continuous casting process it should be possible to bale samples from the melt contained in the upper part of the mould at various stages during the casting of an ingot and thereby determine whether gas absorption is occurring in the casting operation. In this connection I think it is quite likely that gas in the metal before pouring or absorbed during casting would tend to segregate towards the molten pool in the short mould, and tests of the kind I have indicated might well reveal an increasing gas content in the molten pool as casting proceeds. Thus, in the event of gas being detected in the pool only towards the end of the casting process, it would be unwise to assume that gas absorption was occurring only at this stage.

PROFESSOR W. R. D. JONES,‡ D.Sc. (Member): The paper dealing with some technical problems in the rolling of aluminium is very interesting, and a tribute is due to the aluminium industry for the extremely high quality of the sheets produced—a quality resulting from an appreciation of the meticulous care necessary at all stages, from the melting of the metal to the final cold rolling and packaging.

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† W. A. Baker, *J. Inst. Metals*, 1945, 71, 165.

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The hydrogen content of the metal must be controlled and kept to a minimum if porosity in the ingots and blisters on the sheets are to be avoided. The hydrogen content of the molten metal is specific for each temperature, and high temperatures should be avoided. Holding furnaces have an advantage (provided that the bulk is sufficiently large, so that the metal bath can be kept at a relatively low temperature) in that the hydrogen content can be decreased to the equilibrium value. (It cannot go below this value.) The furnace atmosphere is important in this connection, and probably an electrically heated holding furnace will minimize the hydrogen content of the metal by avoiding pick-up from furnace gases and by allowing the hydrogen content to be decreased to that solubility figure for the temperature.

The cooling of the metal after pouring into the mould is an important factor. It is possible that the surface exudations of segregate called "blebs" are due to inverse segregation, and that an alteration in the rate of cooling may minimize this defect.

It is suggested that one of the causes of "crocodiling" is an incorrect microstructure of the ingot. The zone of columnar crystals should be as small as possible, and the grains in the central portion should be equi-axial. The relative amounts of these zones can be controlled by the mould material, speed of cooling, and the relation of the mould wall-thickness to the ingot section. Crocodiling may also arise if at the beginning of rolling the temperature of the slab is too high, so that the strength of the metal is not sufficiently strong to withstand the deformation stresses; while, also, if the temperature be too low, the material is too brittle to withstand the stresses. We have found that the structure of the ingot is probably the most important factor in preventing crocodiling.

Our experience, limited chiefly to magnesium alloys and to a small rolling mill, has been that edges of rolling slabs should be scalped and smoothed as well as the surfaces, and also that if rolling is begun with a few passes of light draft the rolling programme is simpler and more efficient. Even small cracks on the edges readily act as stress raisers and are propagated. We would agree completely with the authors that trouble can be avoided by controlling carefully the casting conditions and/or the slab shape. Once conditions are favourable, each and every operation must be controlled rigidly by severe inspection methods.

Recovery of scrap must be an important factor in large-scale production and a rapid and cheap method of melting is essential. In this connection, it may be mentioned that good results have been obtained with the Sklenar furnace, which, it is stated, can melt large pieces of aluminium alloy scrap without having first to section them. A standard Sklenar furnace of 2 or 5 tons capacity can be used for clean scrap and with a little adjustment of the 5-ton type pieces measuring $6 \times 3 \times 2$ ft. can be readily fed into the furnace. The metal melts in the neck of the furnace flue and runs down the wall of the furnace into the hearth, where it collects until the whole charge is melted. This continuous stream of comparatively cold metal prevents undue overheating of the bath of metal on the furnace hearth. Figures have been given which state that the melting loss obtained, over a period, from a furnace melting all kinds of clean metal, ingots, foundry returns and scrap, is 3.6%, while 6000 lb. can be melted in the large type in 50 min. with an oil consumption of 9 gal./ton. The gas pick-up is no greater than that experienced with crucible melting. If desired, the metal can be degassed in the furnace before teeming, which can be done either from a spout (tilting type) or from a tap-hole in the stationary type.

The remarks on grain-size are interesting. Low-carbon mild steel for deep pressing should have a grain size of 1100-1400 grains/mm.², if good pressing quality is desired with freedom from superficial roughness, commonly known

as the "orange peel" effect. Care has to be taken that a critical combination of deformation and annealing or reheating temperature is not attained, as this would be liable to produce intense grain growth.

Is roller-levelling necessary for aluminium sheets? Its function in mild-steel sheet production is connected with the yield point (and not particularly with flatness)—a phenomenon not met with in aluminium alloys—and it would seem desirable to concentrate on designing a continuous stretching machine. Here again consultation with those who have had experience in the continuous rolling of wide steel strip should be advantageous. Some of the highest-quality rolled sheets in aluminium alloys have been produced by men engaged previously in the steel-sheet trade.

MR. R. A. MILLER * (Member) and DR. K. STRAUSS * (Member): We want to confine ourselves to a few remarks on one aspect of the paper by Messrs Thomas and Fowler and the subsequent discussion, which deals with the fluxing of aluminium and aluminium alloys, particularly strong alloys. In the section on "Blister", the authors state that "Fluxes of the alkali chloride-fluoride types are also difficult to apply and cannot, in any case, be used with strong alloys".

Whilst we can clearly comprehend objections to using such compounds on aluminium-magnesium alloys because of the recognized detrimental influence of sodium above a certain limit, it is difficult to understand the authors' objection to the use of this type of flux on strong alloys, such as the Duralumin variety. Why should they be detrimental—assuming, of course, that the ingredients are thoroughly dried and the resultant product properly packed and stored? Obviously moisture in any form has to be carefully eliminated, but experience shows that fluxes embodying alkali chlorides and fluorides, cryolite, and so on, are widely used in this country and abroad.

This comment applies particularly to large-capacity reverberatory charges, where efficient drossing with the aid of fluxes plays an important part in conserving metal and reducing the dross to a fine powder, when it is readily skimmed off. These fluxes dissolve the oxide film which very often surrounds beads of metal, so allowing the metal to fall back into the furnace bath.

Our contention is, providing always the flux is free from moisture and does not contain any compounds which may introduce unwanted impurities into the metal, that the results obtained can be only beneficial. We except aluminium-magnesium alloys which contain appreciable quantities of magnesium, where the presence of sodium has been proved to be undesirable and the cause of certain failures. This series of alloys is generally "fluxed" with mixtures containing anhydrous magnesium chloride and potassium compounds of the chloride and fluoride type.

Reverting to strong alloys and accepting the fact that in daily practice large quantities of fluxes containing sodium fluoride and cryolite are consumed, it is perhaps pertinent to point out that these fluorides exert a certain dissolving action on alumina. We subscribe to the theory that alumina films have a tendency to "hold" dissolved hydrogen and that consequently, by dissolving this oxide film, greater freedom from gas and therefore greater freedom from blisters can be obtained. This applies irrespective of any separate degassing operation with chlorine, compressed hexachlorethane, nitrogen, &c.

With reference to the degassing of aluminium and aluminium alloys, the authors state that "nitrogen and hexachlorethane do not appear as effective with these strong alloys as they are with magnesium-free alloys. Chlorine appears to offer some advantage." The efficiency of a degassing agent seems not only to depend on the quantity of gas, or compounds which are converted

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to gas, but also on the length of time during which the metal is treated with the agent. In the case of degassing with hexachlorethane (which was introduced by our Company and for which it holds a patent), if the duration of the degassing process is prolonged by application in stages, so that it comes somewhat near to the duration of chlorine treatment, the results obtained are, to our knowledge, in every way as good as, or superior to, those with chlorine or nitrogen, whilst the application is very much simpler. With the right tools, even large, shallow metal baths can be satisfactorily degassed in this way.

DR. R. T. PARKER,* B.Sc., A.R.S.M. (Member): With most of the observations made by Messrs. Thomas and Fowler, I cannot but agree, as they are well founded. But I would call for further enlightenment on one or two points, such as, for example, casting and blistering. I am aware of the cracking of highly alloyed metal when continuously cast into ingot or billet form, and a little work has already been done to determine the size of the stresses set up. I did not before appreciate, however, that cracking in certain alloys is in some cases epidemic without apparent cause, although other contributors to this discussion have mentioned cracking associated with the presence of undesirable impurities. My own view of this, for what it is worth, is that in the continuous-casting process, we have a method which is far more sensitive to change than the old permanent-mould method, and that we are dependent upon the skill and "know-how" built up by the teams of operatives upon each unit. When, through one or another reason such as fatigue, working conditions, &c., there is any deviation from the optimum conditions for successful casting, trouble may arise. In the casting of the highly alloyed metals into ingots the result may be cracking. The authors themselves have listed a number of factors which are also known to affect castability, and it is not difficult to appreciate the permutations and combinations of these which may subsequently be worked through to find out the reason for cracking.

In any case I would put fairly far down the list the suggestion that abnormally high gas contents and oxides are at the bottom of such epidemic cracking when normal good-quality metal is used. Scrap metal may need different treatment.

Another observation on the results of casting is contained in Section III, under scalping, where the factors affecting smoothness of the ingot surface are given. I would agree that reduction of speed, metal depth, mould design, method of applying water, &c., all have some effect, but would it not be truer to say that the main factor is the rate of removal of heat, and that the aforementioned factors all affect this rate? The air gap between ingot and mould and its size and rate of generation are linked with all the above factors, including that of heat removal, and the air gap may offer a means of gauging the effect of variation of these factors. This, I believe, is an interesting aspect of this method of casting, and one which will repay study. The authors have implied this in their conclusions, where they stress the need for higher casting speeds.

The authors did not mention that multiple continuous casting of ingots and billets is one way of increasing casting speed, although this does not raise the rate of heat extraction in any one casting, which may be advantageous from a structural point of view.

The observations upon blistering are also of great interest, and I would like to make a few comments on them. The authors suggest that a blister starts from a cavity containing some gas, but I feel that they would agree that all that is needed is a discontinuity in the first instance towards which gas may diffuse and build up a pressure. Similarly, in the same paragraph they seem to say

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that the effect of rising temperature alone may be enough to generate sufficient pressure for blistering, and I would suggest it is necessary to envisage the simultaneous diffusion of gas into the metal at the discontinuity to give the required pressure. This gas may or may not be in solution in the metal and it may be derived at a later stage from heat-treatment furnace atmospheres. Again, on p. 928, I would refer to the statement that melting furnace atmospheres have little influence on hydrogen pick-up, where I believe the authors mean that *excessive* gas contents, over and above the equilibrium amounts, are derived from contaminated metal.

In reading the very interesting Sections upon temper control and grain-size, and in referring to the observations made in the Conclusions on the same and other problems, I note the authors' reluctant conclusions that statistical analysis has not proved a very helpful aid. Perhaps their disappointment is due to the fact that in production the number of factors upon which data must be collected for the statistical attack on any one problem is so large that very complete and continuous records should be kept. Nevertheless, under pilot-plant conditions we find no difficulty in planning experiments upon this subject of grain-size and recrystallization characteristics which will investigate six or seven factors at once, in the belief that we obtain useful data on the main factors and interactions which are worth verifying under larger-scale conditions.

As a general comment, I would say that the authors have drawn attention to some of the main problems which must receive the attention of metallurgists and engineers in the aluminium industry to-day. I would agree that users of aluminium alloys in all forms are asking for material of even better and even more consistent quality, whether these qualities are reflected in mechanical properties, grain-size, or finish. There is a simultaneous tendency to much closer composition control, and with some of the alloys, this means a greater use of high-quality virgin pig metal. It is worth while pointing out, however, that there are means of attack on the problem of cheapening the final product which have not been mentioned. Why do we waste the heat energy in molten metal by chilling on casting and then re-heat for working purposes? The Hazlett process for direct strip rolling offered some solution to this problem, but also possessed some disadvantages of its own.

MR. R. B. SIMS *: Messrs. Thomas and Fowler have made an admirably clear statement of the problems yet to be solved in the rolling of aluminium and its alloys. Their remarks on the properties of rolling oils are particularly valuable, since very little systematic research has been done on this problem.

Several materials have been rolled recently with various rolling lubricants on the B.I.S.R.A. two-high 10-in. experimental mill, and from measurements of the roll-separating forces and torques an estimate has been made of the variations in the coefficient of friction (μ) between the rolls and strip. It has been found that μ varies in a random fashion from pass to pass and also, to a smaller extent, during a single pass. Results of experiments on mild steel rolled with a 10% solution of soluble oil in water indicated that μ had varied between 0.08 and 0.05. Since the roll-separating force varies with μ , and the mill frame elongates as the roll force increases, it is clear that a change in the coefficient of friction during a pass will result in small changes in the thickness of the rolled strip. At reductions of 30-40% on annealed strip of the softer metals such as copper and aluminium, this effect can produce variations in gauge which may be unacceptable commercially. One requirement of the rolling oil, therefore, is that it should give constant frictional conditions in the roll gap.

The need for a constant value of the coefficient of friction emphasizes also

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the need for adequate roll cooling. The mechanism of the lubrication in the roll gap is probably of the boundary type. Since boundary lubrication breaks down at comparatively low temperatures, depending upon the lubricant, the strip material, the pressure in the roll gap, and the roughness of the surfaces in contact, it follows that if constant frictional conditions are maintained the rolls must be cooled so that this limiting temperature is not exceeded in the roll gap. The second requirement of a rolling oil is that it functions at relatively high temperature and pressure.

Chertavskikh * in discussing the relationship between the lubricating and staining properties of an oil, has pointed out that, in general, staining increases with lubricity, and that, when used on soft metals non-staining lubricants such as kerosene are of such poor lubricity that plucking and tearing takes place between strip and rolls, giving a poor surface on the rolled strip which reduces its market value. Hence a third requirement of the rolling lubricant is that it neither stains nor impairs the surface finish of the strip.

It would be of interest if the authors would describe in more detail the method used to control variations in roll camber due to temperature differences. Perhaps the most satisfactory solution to both lubrication and camber problem would be to use a soluble oil and water emulsion as a flood lubricant and roll with the roll-separating force maintained constant by the variation of strip tension, since a constant value of the roll-separating force would keep both camber and strip thickness sensibly constant. There is an urgent need, therefore, for a lubricant with the specification mentioned above which will act as the coolant.

MR. W. J. THOMAS and MR. W. A. FOWLER (*in reply*): In replying to the various interesting written comments on our paper, we shall also take the opportunity to deal further with several points raised at the Paris meeting.

In order to maintain ease of reference, our further replies are grouped under the section headings used in the paper.

Casting.

We are interested in Dr. Parker's comments and agree that the phenomenon of slab cracking in the case of strong alloys is, to a certain extent, unpredictable and susceptible to such factors as fatigue, working conditions, &c. There is need for closely controlled conditions, and we expect that the interaction of the several variables operating in semi-continuous casting may take some time to resolve.

Scalping.

With regard to Mr. Smith's remarks, trials of the German vibrating process have not shown it to be entirely satisfactory in giving absolutely smooth slab surfaces, while the bucket mould mentioned by Mr. Smith appears to have been outmoded by the semi-continuous casting process.

We have found that a small downward inwards taper in a semi-continuous casting mould does give rise to a slightly improved appearance, but does not eliminate exudation in pure metal nor the evidence of inverse segregation in alloys, and cannot, therefore, be regarded as a means of avoiding scalping.

In reply to Professor Jones's written remarks, it can be said that in semi-continuous casting the formation of the banded exudations experienced principally with pure metal is caused by a periodic melting through of the first-solidified shell of metal. In our experience the bands of exudations occur at a vertical spacing down the length of the slab of about 3 in. and are surprisingly regular, having no relation to the thickness of the slab within the range normally cast.

* *Zhur. Tekhn. Fiz.*, 1944, **14**, 555.

The cause is undoubtedly due to a thermal oscillatory condition; during casting the metal shrinks away from the mould as it solidifies and the heat extraction through the mould wall is thereby diminished, incipient melting takes place in a horizontal band and the sac of molten metal re-solidifies when it touches the mould. The band is thus formed and the process repeats itself.

In the case of magnesium-bearing and strong alloys, there is a uniform rough surface on the slab owing to inverse segregation.

Multiple semi-continuous casting is often used for reasons of economy, but this does not control the rate of descent of the slab or billet and therefore does not, in any way, help to overcome the type of surfaces experienced.

Blister.

Mr. Bowman raised the question of degassing technique. It is true that the large shallow baths normally used with semi-continuous casting units are not very convenient for degassing, and there is a problem presented here.

The efficiency of degassing depends upon the depth of metal traversed by the bubbles of the degassing agent, and for this reason it is desirable, and advantageous, to have the bath as deep as is compatible with other considerations. If the bath area is large, it is also difficult to ensure uniform distribution of the degassing agent.

For this latter reason we consider it is undesirable to introduce the degassing agent from fixed points, as is suggested by Mr. Bowman, and prefer introduction by a perforated ladle, or similar tool, which can traverse the liquid bath.

Mr. Smith dealt with this point when he indicated that the efficiency of degassing operations is very much a function of the way in which they are carried out in practice. For instance, metal temperature is one of the most important factors and one which, in practice, is somewhat difficult accurately to control.

Choice of agent is also an important factor. Fluxes of the Hanson and Slater type can produce beneficial results with pure metal and certain alloys but, in the case of magnesium-bearing alloys, there is a danger of sodium absorption occurring to such an extent as to affect the working properties of the alloys.

The reason for the deleterious effect of sodium in such alloys is not clear, but we might add that there is no evidence to suggest that the effect is due to gas pick-up during processes subsequent to casting.

Mr. Smith asks whether if two melts, one of high gas-content and one of low gas-content, properly degassed, would vary in gas-content after degassing. The answer is no, if the degassing is thorough; the rate of removal of gas is quite rapid when the gas-content is high and the gas-content curves of the two melts would rapidly converge. If an efficient and reliable method of degassing is available, therefore, it would appear on first sight that expensive precautions in melting practice are unwarranted, but gas content is not the only factor affecting metal quality—factors such as oxide content must also be considered.

Mr. Smith's suggestion that surface channels due to milling may cause blister is in accordance with our experiences, and on p. 927 of the paper we draw attention to the need for a good surface on rolling slabs.

Mr. Baker has dealt with possible sources of gas content. We would say that although blisters can occur in metal melted under an oxidizing atmosphere, it is true that use of a slightly oxidizing flame is the better procedure, and we agree that direct impingement of the flame on the bath surface should be avoided, especially with oil fuel, though this is not easy to achieve.

The pick-up of gas from the atmosphere is not nearly as rapid as once was

thought, and with degassed metal we have not noted any evidence of an important rise in gas-content in transfer of metal from furnace to mould, or during semi-continuous casting. Laboratory measurement has not shown a rise in gas content with metal cast by the semi-continuous process; nevertheless, it is known that serious deterioration can, and will, occur if damp launders or damp ladles are used in the transfer process.

At the low level of gas content at which it is necessary to work in the semi-continuous casting of rolling blocks, there appears to be no appreciable segregation of gas to the residual pool of molten metal, and examination of the solidified slab has indicated uniform distribution of gas from top to bottom, thus bearing out the view we have expressed.

While Professor Jones is correct in drawing attention to the importance of temperature in the bath, he appears to be under some misapprehension with regard to the relation between the normal gas content of molten aluminium and aluminium alloys and the solubility of hydrogen at various temperatures.

The amount of gas present is usually very much below the equilibrium solubility at one atmosphere pressure; the metal is never supersaturated in the way Professor Jones implies.

Mr. Miller and Dr. Strauss have been answered in our reply to Mr. Smith, but we may add that they appear to have overlooked the point that alkali chloride-fluoride fluxes cannot conveniently be used in reverberatory furnaces because of the attack on the furnace lining.

The comment made by Dr. Parker on the mechanism of blister formation is, of course, quite valid. There must be diffusion of gas from the metal into the pore, and this is an important factor in determining the blowing up of blisters.

Scrap Remelting.

In further reply to Mr. Bowman, we confirm that the furnace suggested for scrap remelting is of the duplex type, with a large charging hearth on which the charge is preheated to almost the melting point, and it passes thence to an adjoining melting hearth at a lower level.

Mr. Thornely raises an interesting point when he refers to the possible use of induction melting. While it is recognized that a reverberatory or open-hearth type of furnace, with or without a charging or liquation hearth, gives rapid and economic melting over the range 5-15 tons capacity, we feel that the development of induction melting may lead to useful new methods in this country. Induction melting has been practised in Germany, and it appears that the use of energy is most efficient, although not necessarily at the cheapest fuel cost, but there does seem to be lack of versatility with induction furnaces when the call is for the recovery of scrap from a number of alloys.

Professor von Zeerleder referred to this problem of versatility when he indicated that induction furnaces are normally emptied once a month.

Hot Rolling of Strong Alloys.

We have given further consideration to the very interesting points raised by Mr. Hessenberg, and we have consulted the original paper by Baker, Ricksecker, and Baldwin to which he refers. These authors worked on brass ingot and were studying cold rolling. It seems to us that the surface stresses to which they refer would most probably be relieved in the hot rolling of aluminium alloys, particularly in the earlier stages when crocodiling is most liable to occur.

Nevertheless, we feel that the phenomenon of crocodiling is explicable on the general assumption that stresses generated by the rolls are the cause

of the trouble, and we would draw attention to the paper by Kasz and Varley * published in the January issue of the *Journal* of the Institute.

With regard to the edge cracking, we are sure that Mr. Hesseberg is correct in attributing much of the trouble to the shape of the edge, and we were glad to see that the figures quoted by him confirmed our views in this matter.

In hot rolling strong aluminium alloys, the edges tend to become rounded, but concave rather than convex, due in part to the early widening passes. But one would expect the effect to be precisely similar to that described by Mr. Hesseberg, as, owing to the shape, the edge will not be rolled but stretched to keep pace with the rest of the strip.

Both Mr. Thornely and Mr. Smith raise the question of the effect of impurities, in particular sodium, on the behaviour of alloys during hot rolling. While we agree that some minor impurities, if present to the extent quoted by Mr. Thornely for lead, may have a very serious effect, we must point out that detailed laboratory examination of innumerable samples of crocodile rolling slabs has proved fruitless in the search for positive evidence of the effect of small quantities of minor impurities. While not disagreeing with the view that sodium is an element subject to suspicion, we must add that all our evidence leads us to conclude that the amount of sodium normally present in virgin ingot (say 0.003% max.) is quite harmless.

Professor Jones deals with problems related to chill-cast slabs. The microstructure of semi-continuously cast slabs is quite different, but both chill-cast and semi-continuously cast slabs can crocodile. Experiments with specially cut block sections have shown that crocodiling can occur on a plane at right angles to the major casting axis when the sections are rolled with such a plane parallel to the rolling direction.

Roll Cooling and Lubrication.

Mr. Bowman and Mr. Sims have both dealt at some length with the very important questions of cooling and lubrication.

Filtration of soluble oil emulsion would be advantageous, but this additional step must be weighed against the increased cost. We also agree that soft water is very desirable in making up soluble oil emulsions, but we feel that soft water is required more for the stability of the emulsion and the control of the coating on the rolls than for the elimination of staining of the stock, a trouble not normally associated with hot rolling in our experience.

To diverge for a moment, we would mention that the use of hard water for quenching and washing after heat-treatment can cause staining, and in view of the large quantities used in these operations, softening processes are not practicable; but we feel that work on promising addition reagents would bear fruit.

Mr. Bowman rightly stresses the need for the closest co-operation with the oil industry so that the best possible cold-rolling lubricant may be developed, and we agree with Mr. Sims in the view that there is need for fundamental work to establish the characteristics of a good rolling lubricant. Until such work is successfully concluded, the present rather empirical approach must be maintained with all its enthusiasms and disappointments.

Whilst we agree that, in general, lubricity and staining tend to be antagonistic, we have observed that there are exceptions to this statement. We have noted that supplies of oils with organic phosphorus derivatives as additives show remarkable freedom from staining and moderately good lubricating properties, but such oils give rise to objectionable fumes. This observation gives grounds for hope that an unobjectionable non-staining lubricant and coolant may yet be achieved.

* F. Kasz and P. C. Varley, *J. Inst. Metals*, 1949-50, **76**, 407.

Mr. Sims has asked about control of camber, but we feel that this very specialized subject merits individual, and perhaps lengthy, discussion, and we would mention only that some control can be achieved by concentration of sprays at the high points.

We do not favour Mr. Sims' suggestion that soluble oil-water emulsion is likely to be the most satisfactory flood lubricant for the cold rolling of aluminium. Such emulsions can cause serious staining of the bright surface of the aluminium. On the other hand, the use of a soluble oil emulsion applied to the rolls by means of cooling boxes or pads in conjunction with a rolling lubricant drip feed to the strip presents some problems. In particular, the pads must be kept sufficiently tight to allow enough circulation of soluble oil to give adequate cooling without leakage of the soluble oil.

Temper Control.

Mr. Bowman puts forward the attractive idea that the difficulties in annealing and temper rolling to half-hard and three-quarter-hard tempers should be overcome by using modified alloy compositions to give the same equivalent strength in the annealed condition. Unfortunately, there are other aspects than strength (we assume Mr. Bowman means ultimate tensile strength) to be considered, and these affect the choice of the alloy for particular uses. It would therefore not be practicable to overcome normal rolling difficulties in the way suggested.

Grain-Size.

Professor Jones has referred to the production conditions observed for good pressing quality in mild-steel sheet, particularly fine grain. The relationship between deformation and annealing for aluminium was the subject of work by Carpenter and Elam* and later workers in this field, and as a result of such work optimum rolling conditions have been evolved. To mention only one aspect, it is common practice when rolling pure aluminium and the 1.25% manganese alloy (N.S. 3 in B.S. 1470) to employ a heavy cold reduction of 66-75% before an anneal.

Dr. Parker has commented on the use of statistical analysis in connection with grain-size and recrystallization characteristics, and we think he has misinterpreted our view. It was not our intention to suggest that statistical methods are of no value. What we had in mind was the danger inherent in the blind use of statistical analysis without full appreciation of the underlying metallurgical factors involved. If statistical analyses are so used they can lead to erroneous conclusions.

We have, in the past, carried out many experiments on a full production scale which have been planned and analysed on a statistical basis, and these have given very useful results. But this is a very different procedure from the application of statistical analysis to the examination of day-to-day records of performance or routine returns of test results. When the results come from day-to-day operations, much more care and knowledge of the process is needed if useful and reliable results are to be achieved.

Conclusion.

Dr. Parker refers to the apparently uneconomic dissipation of heat inherent in semi-continuous casting. The cheapness of the casting method and the ability to cast large rolling units outweigh the heat loss.

We would agree that the Hazelett process for direct strip rolling appeared to offer some solution to the problem, but the Hazelett process also possessed distinct disadvantages of its own, as Dr. Parker has remarked.

* H. C. H. Carpenter and C. F. Elam, *J. Inst. Metals*, 1921, 25, 259.

DISCUSSION ON PAPER BY PROFESSOR A. M. PORTEVIN AND M. M. DANNENMULLER : "SEGREGATION AND LIQUATION OF ALLOYS AND THEIR APPLICATION TO NON-FERROUS METALLURGY." *

(*J. Inst. Metals*, this vol., p. 949.)

MR. W. H. RICHARDSON † (Member) : I wish to make a few comments on the question of segregation in copper-tin alloys. We have in the past seen many references to the question of inverse segregation, commonly known as "tin sweat", and various theories have been advanced to account for it. However, I feel that insufficient attention has been paid to the effect of the gas content of the alloys in question and that the pressure exerted by this gas during solidification has a major effect on inverse segregation.

In more recent years, we have seen many processes developed for the elimination of gas from tin bronzes, particularly by Dr. Lepp in France and more recently by Dr. Pell-Walpole at Birmingham and by Mr. Baker and his colleagues at the B.N.F.M.R.A. As a result, I feel that most members of the industry will agree that the question of inverse segregation in tin bronze castings and chill castings has largely disappeared, and we have very few problems of that type nowadays.

I wonder whether the authors could give us any information on the effect of phosphorus on the freezing range of copper-tin alloys. I think it is generally agreed that phosphorus does increase the freezing range, and in particular the high-phosphorus alloys are very prone to inverse segregation.

MR. E. A. G. LIDDIARD, ‡ M.A. (Member) : In my opinion it would have been desirable if this paper could have been discussed jointly with that recently published in the *Journal* by Dr. Adams, § because that paper puts rather a different interpretation, or at least a different emphasis, on some of the factors responsible for segregation, and inverse segregation in particular.

The first and most important difference between the paper by Dr. Adams and that by the present authors is with regard to the effect of volume change on solidification in determining whether segregation will be direct or inverse. Adams showed experimentally that under conditions of unidirectional solidification from a chilled face inverse segregation took place in a gas-free aluminium-copper alloy, and that this segregation was accompanied by an increase in the number of voids. Adams favours the explanation that this segregation is due essentially to the flow of eutectic-rich liquid to compensate for solidification contraction, and in proof of this he showed some experimental results on a bismuth-6% tin alloy which expands on solidification. The segregation curve was exactly the reverse of that obtained with the aluminium-4% copper alloy, which contracts on solidification. In directionally solidified

* Discussion at the Annual Autumn Meeting, Paris, 5 October 1949.

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§ *J. Inst. Metals*, this vol., p. 809.

chill-cast ingots of this material there was a comparatively high copper content near the chill face and then a zone where the copper content was slightly above the average composition, and finally at the top of the ingot, where the feeding took place, the copper content fell, the voids curve was almost a mirror image of the other one, and a decrease in copper content was reflected in an increase in percentage voids in the casting. On the other hand, with bismuth-6% tin alloy, which expands on solidification, there was an impoverishment in tin at the chill face and an enrichment at the top of the ingot which was the exact opposite of what was obtained with the aluminium-copper alloy.

The other point which Adams makes—and I think it is obvious from this theory—is that if the rate of solidification is such as to maintain an adequate differential between the ratio of rates of diffusion in the solid and liquid—and that, of course, is very important—then it follows that it is the directionality of solidification rather than the speed which is important. Nine times out of ten, in order to obtain marked directionality, one cannot avoid having comparatively rapid solidification, but it is the directionality rather than the speed which is important. Adams showed experimentally that the degree of inverse segregation was not critically dependent on the rate of solidification.

I should therefore like to suggest that to the principal factors which the authors list at the top of p. 960 as promoting inverse segregation we should add "Volume changes on solidification and directionality of solidification", and I also suggest that "the form of crystallization", except in so far as this is affected by directionality, should be omitted from (1) in the first paragraph on p. 960, because this mechanism is obviously not dependent on crystal size. Adams showed this experimentally, and he found that alloys of similar composition, but with a grain-refining addition of titanium in one case, gave exactly the same degree of segregation, though the grain-sizes and crystal structures of the solidified ingots were very different.

I entirely agree with the present authors in their assessment of the part played by gas in segregation, though I have a good deal of sympathy with Mr. Richardson when he mentions the enormous importance of gas on a practical scale. I do not think that gas is an essential factor in segregation phenomena, though in practice its presence can exaggerate inverse segregation to such an extent that very often if the gas is removed all the troubles disappear in practice. I should like to point out, however, that the gas itself is showing normal or direct segregation, because normally the gas is more soluble in the liquid than it is in the solid, and the gas which is rejected on solidification of the first-formed primary crystals will tend to diffuse into the remaining liquid until the gas content reaches the solubility limit. At that stage, particularly if the liquid is in movement, the gas will be released and will set up a pressure inside the solidifying ingot which will force the remaining liquid metal through discontinuities in the solid skin, and so you get the blebbing and exudations which are so troublesome in practice.

The authors give some most interesting examples of refining, based mainly on gravity segregation. We are not unfamiliar with that in the light alloy industries, and during the war much attention was paid to the removal of impurities in aluminium and its alloys by gravity segregation or by filtering the primary crystals away from the pasty mass. A good deal of work was done on this at the British Non-Ferrous Metals Research Association, and even more was done in Germany. Probably the most interesting process, which is known to nearly all of us, is based on the addition of magnesium to aluminium to form the low-melting-point and relatively pure aluminium-magnesium eutectic in which the solubility of iron is quite low, and the separation of the iron-rich primaries by gravity segregation. Subsequently the magnesium is removed by distillation. There is also, of course, a similar process based on zinc. In these

days of rising metal prices and diminishing mineral resources, efficient methods of purifying and separating undesirable impurities from scrap metal become of more and more importance, and I think that the authors deserve our thanks for drawing attention to the very important part which liquation can play in such processes.

MR. J. CARTLAND,* M.C., M.Sc. (Vice-President): I want to discuss only one point, and that is the function of copper in reducing or preventing the segregation of the other constituents in tin-base and lead-base white metals, which is mentioned in the paper on pp. 956 and 957.

The function of copper in tin-base white metals is clear and well understood. It was described adequately as long ago as 1920 by Hudson and Darley.† Feathery crystals of copper-tin needles separate throughout the melt, and they entangle and enmesh the subsequently-formed tin-antimony crystals and prevent them from floating to the surface. When we come to the lead-base alloys, however, the mechanism is not so simple and not so well known. At the bottom of p. 956, the authors say "Alloys of lower lead and tin content (e.g. less than 5%) require only 1% copper addition to form a mesh of slender Cu_2Sb needles which prevent segregation of antimony crystals". It is not clear from the text what is the composition of the alloys which the authors were considering in the opening part of that sentence, but a very important point arises in the latter part of that sentence, when they refer to "slender Cu_2Sb needles".

In our experience, where copper occurs as a copper-antimony compound it always occurs in the form of flat flakes, which are very different from the feathery copper-tin needles. In that sense, our observations are at variance with those of the authors. The function of copper in lead-base alloys is one of concern to us, because copper occurs in printing metals, generally as an impurity but occasionally as an intentionally-added constituent, while in lead-base bearing metals copper usually occurs as an intentional addition, with the object of minimizing the segregation of the other constituents.

We therefore investigated the occurrence of copper in lead-base white metals. We took an alloy of the general composition tin 10%, antimony 10%, copper 1%, and the balance lead, and we varied the tin : antimony ratio and observed the results. They showed that when the tin was in substantial excess of the antimony the whole of the copper appeared as the feathery copper-tin needles. On the other hand, if the antimony was in substantial excess of the tin, the whole of the copper came out in the form of these flat flakes, and none in the form of needles. With intermediate compositions both sets of crystals could occur, but the copper-tin ones were always needles and the copper-antimony ones always flakes.

It is somewhat strange that the copper-antimony flakes are as effective as copper-tin needles in preventing segregation. Perhaps the authors can explain the variations of crystal form by reference to the quaternary diagram concerned.

Note added in proof: The above figures were quoted from memory. On referring to the original work I found that we took a lead-base alloy with 15% antimony and 1% copper and varied the tin content from 10 to 20%. We found that with less than 11% tin the whole of the copper was in the form of copper-antimony flakes; with more than 14.5% tin the whole of the copper was in the form of copper-tin needles; in the intermediate range, both types of crystal were present.

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† *J. Inst. Metals*, 1920, 24, 361.

M. DANNENMULLER (*in reply*): Mr. Richardson raised the problem of the influence of gas in promoting inverse segregation. It is possible that in some cases gas is responsible for this segregation, but I would point out that in the preparation of metals the utmost care is taken to avoid the inclusion of gases during melting, simply because of the enormous difficulties involved in getting rid of them afterwards. To take an example from copper metallurgy, I would quote the making of alloys for bearing linings, where every precaution is taken to avoid the inclusion of gases. What we suppress in this way is not the inverse segregation but one of the factors which cause inverse segregation, and in spite of all these precautions inverse segregation continues to occur. I believe that, as we have said in the paper, gas may have the effect of exaggerating inverse segregation, but if the necessary precautions are taken industrially to avoid gases being taken up, their action in this respect will be minimized, but we shall not exclude all the factors responsible for inverse segregation.

Mr. Liddiard mentioned a certain number of cases which demand careful study. I believe that there is no one absolute or universal cause of inverse segregation. We shall be interested to study the examples cited by Mr. Liddiard in detail, because it is possible that different factors are coming into play, and there is no one simple cause for the segregation referred to or for the phenomenon mentioned, which seems contrary to generally accepted ideas. Very often the appearance of two or three factors at the same time gives an unexpected result, and I think that inverse segregation ought to be studied separately for each alloy. For example, with the type of lead bronze alloy to which I have already referred I may say, without going into details of the experiments which we have carried out, that we are persuaded that the important factor is the contraction of the layer of copper which solidifies initially, and here the phenomenon of contraction is mainly responsible for the inverse segregation; but this is only one case out of many, and it is certain that many other cases must be regarded very differently.

Mr. Liddiard said that in the cases which he had observed he did not see the influence of the form of crystallization on inverse segregation. In the examples he cites that may well be so. He speaks of segregation produced when the solid was continuous and the liquid was discontinuous. That differs fundamentally from the case where the liquid is still continuous and the crystals have a discontinuous form. It is certain that the experiences which he mentions show that the size of the grain and the form of crystallization are of comparatively little importance when the inverse segregation is produced in the last stage of solidification.

In reply to Mr. Cartland, there is a very simple method of distinguishing between the CuSn and Cu_2Sb needles, and that is to examine them under polarized light, when the Cu_2Sb shows a violet appearance which cannot be mistaken. We are carrying out in our laboratory work on the quaternary system lead-copper-tin-antimony which goes beyond what is reported in the paper, where we have simply given a few results obtained on anti-friction alloys without entering into details or making more precise the zones of crystallization and so on and the different results obtained in regard to segregation according to whether one is dealing with CuSn or Cu_2Sb . It is interesting to prepare large single crystals with a length of several centimetres and to compare what are called the needles of CuSn with the flakes of Cu_2Sb . One finds that in reality there is not a big difference in general geometrical aspects between the two compounds.

CORRESPONDENCE.

DR. W. J. KROLL * (Member) : The excellent review given in this paper on the segregation and liquation of alloys, as well as the appendix by M. Jollivet, give the reader the general theoretical ideas underlying the problems involved in alloy separation. No attempt was made, however, to deal also with the equipment used in such operations. The bibliography given is rather sketchy, and it does not in most cases go back to the original publications of the discoverers of the processes described. This objection applies particularly to the production of aluminium-silicon alloys in the arc furnace and the Kroll-Betterton process for the debismuthizing of lead. The few examples presented by the authors do not include important recent achievements, though they may support adequately their theoretical viewpoints. Moreover, the thermochemistry of intermetallic compounds, which plays an important role in metal-separation processes, has been ignored.

As far as equipment goes, a discussion of the classical tools of liquation, namely, kettles, reverberatory furnaces, liquation hearths and the Howard press, in relation to the theories expounded would have been welcome. Modern filtering methods using a refractory bed, which appear to have such a bright future, have been left out entirely.

The most important omissions from the bibliography concern the carbothermic process for the reduction of clay by the Horrem method, which yields aluminium-silicon alloys, and the debismuthizing of lead with calcium. The most essential of the missing references are given below. They concern the German Horrem process for filtering aluminium-silicon alloys †; the use of calcium, magnesium, and alkali metals for debismuthizing lead; ‡§ the use of sodium to eliminate antimony, arsenic, selenium, and tellurium from alloys in general, and from those of lead, tin and copper in particular; ¶§ the substitution of aluminium for alkali and alkaline earth metals in these separations, especially in the treatment of solder; §|| the de-antimonizing and de-arsenizing of lead and tin alloys with zinc after preliminary removal of any copper.¶ These old references cover most of the field claimed by M. Jollivet for his "dissociations".

A number of erroneous statements as to the calcium debismuthizing process have been noticed. The combination of calcium and magnesium for debismuthizing lead was not discovered in Germany, but in the United States, by J. O. Betterton. It permits the final bismuth content of 0.05%, obtained by the Kroll calcium process, to be reduced to 0.02%. Addition of antimony after the calcium-magnesium treatment brings the bismuth content down to the 0.001% limit. This, too, is one of Betterton's discoveries. Oxidation of the refined lead to eliminate calcium, as shown by the authors' flowsheet, was never used in any plant so far as we are aware, the lead losses being too high. These can be avoided by chlorination, which yields a liquid, lead-free slag. The bismuth skimmings can be treated by liquation, which brings the bismuth content well above 60%. A chlorine treatment eliminates the calcium in them, as well as the lead content, in two steps, if required. It would be out of place to discuss here why preference is given to the electrolytic treatment of the

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† V. Engelhardt, "Handbuch der technischen Elektrochemie". Leipzig: 1934, p. 374.

British Intelligence Objectives Sub-Committee, *FIAT Rep.* No. 253.

Anon., *Metal Ind.*, 1947, 71, 447, 467.

‡ W. Kroll, U.S. Patent No. 1,428,041, 1922; German Patent No. 410,533, 1925.

§ W. Kroll, *Metall u. Erz*, 1922, 19, 317; 1933, 35, 1.

¶ W. Kroll and Th. Goldschmidt A.G., German Patent No. 423,245, 1925.

¶¶ W. Kroll and M. Lissauer et Cie., German Patent No. 487,431, 1929.

calcium-free bismuth skimmings instead of concentrating them by liquation. No Pb_3Ca is formed in debismuthizing with calcium as long as the bismuth content is above 0.05%, but any calcium in excess of the compound Bi_2Ca_3 forms Pb_3Ca first, later PbCa , and then PbCa_2 with more calcium. If debismuthizing to the 0.05% limit is desired, a slight excess of calcium is necessary to produce a Pb_3Ca mass, which collects the fine Bi_2Ca_3 crystals. Two recent publications give the information about the mechanism of the debismuthizing process * required by the authors. The Pattinson process for debismuthizing and desilverizing lead is found only in text-books, as an historical curiosity. Its value in teaching is, however, considerable.

The field of metal-separation processes, as shown by the references given below, is much broader than might be suspected. We mention the separation of copper and nickel contained in tin alloys, after adding lead, with silicon as precipitating agent,†‡ analogous with the Haertling process described by the authors for the iron-tin series. There is also the layer-separation process in the systems $\text{FeS}-\text{FeSi}$, $\text{Cu}_2\text{S}-\text{FeSi}$, and $\text{Al}_2\text{S}_3-\text{FeSi}$,† the last-named being the basis of the Haglund alumina process. The separation of zinc from galvanizing residues by aluminium † and the elimination of titanium from aluminium by nitrogen may be mentioned too.† The refining of magnesium by adding manganese to bind the iron, or the co-precipitation of silicon,† iron, and manganese in magnesium † belong in the same group of reactions. Elimination, as shown by these examples, is not always necessary to obtain a metal having suitable physical properties, and neutralization of the harmful element may meet all requirements, as demonstrated by the neutralization of traces of bismuth in copper by adding calcium. This list is far from complete, even after including the very important war-time developments in Germany for refining aluminium scrap by dissolution in mercury, lead, magnesium or zinc, and filtering the compounds formed on a refractory bed.§

The zinc process for the elimination of antimony contained in solder,|| described by the authors, was used successfully for a number of years. It is true, that when reducing the antimony in the refined metal below 0.2%, the zinc consumption increases. This method was abandoned not because the results of de-antimonizing were poor, but because the by-product, 40% antimony alloy, could not be worked up economically. This shows that the problem of the by-product treatment may, in some instances, become the controlling factor.

As to the merits of the debismuthizing process described by M. Jollivet, his vague sentence "the lead so treated will probably contain less than 0.005% bismuth" will not satisfy any lead metallurgist, considering that, for certain applications, thousandths of one per cent. bismuth count.

The use of alkali, alkaline earth metals, and aluminium for the elimination of alloy constituents involves a great health hazard, if arsenic, selenium, tellurium, or phosphorus is present even in small quantities. Arsine poisoning from the dross obtained in de-antimonizing solder containing less than 0.2% arsenic with aluminium as a reagent can be expected and many fatal accidents all over the world have been reported from handling such materials.¶ Arsine forms quite readily from this dross by reaction of the arsenide with moisture from the air or by spraying it with water or exposing it to rain. Methods have been developed to neutralize such very dangerous products, for instance, by

* D. Evers, *Z. Erzberg. u. Metallhüttenwesen*, 1949, 2, 129.

H. Grothe, *ibid.*, p. 177.

† W. Kroll, *Metall u. Erz*, 1938, 35, 1.

‡ J. O. Betterton and Y. E. Lebedeff, U.S. Patent No. 2,329,817, 1944.

§ Anon., *Metal Ind.*, 1947, 71, 447, 467.

|| W. Kroll and M. Lissauer et Cie., German Patent No. 487,431, 1929.

¶ E. H. Kohlmeier and H. H. Pontani, *Z. Berg-, Hütten- u. Salinenwesen*, 1935,

roasting them on the spot in air.* Even sodium arsenide drosses can be handled in this way. The silicides containing arsenic may not be quite so dangerous, but care is recommended.

In spite of these few criticisms, the authors have well served the cause of metallurgy by arousing the interest of plant operators in certain problems of physical metallurgy that have, up to now, received little attention.

The AUTHORS (*in reply*): Dr. Kroll's interesting observations fall under three headings: (1) Bibliography, (2) Industrial plant, and (3) Discussion of processes.

(1) *Bibliography*.—With such a wide subject as that, with which we have been dealing, it would have been impossible, without overburdening the text, to give all the bibliographical references. We are aware of the numerous researches carried out by Dr. Kroll in certain fields of refining, and the many interesting papers he has published would certainly be included in a complete bibliography. However, we should have had to list several hundred papers in order to refer the reader to all the original work on the subjects we have touched upon in our paper.

(2) *Industrial Plant*.—We purposely omitted an account of the industrial plant required for the successful large-scale application of the segregation and liquation processes to the refining of metal. It was not thought of sufficient interest to reproduce the conventional descriptions of the ordinary equipment. On the other hand, it does not appear that filtration processes have introduced any very novel features into the subject under survey. These filtration processes were already outlined in very early patents and they have certainly been improved since then. But it is not possible to publish information on the most up-to-date procedures, which the industry would rather not see disclosed.

(3) *Discussion of Processes*.—A detailed account, with complete bibliography, of the production of aluminium-silicon alloys by thermal means and of the elimination of bismuth from lead, would have required as much space as the whole of our present paper. Therefore, in order to emphasize the theoretical and instructive aspects, we have been obliged to concentrate on the main outlines of each process. The Horrem process, for example, is not the only one suitable, and it would no doubt be a difficult matter to decide in which country the idea really originated of the manufacture of aluminium-silicon alloy by producing silico-aluminium in an electric furnace and then eliminating the silicon by segregation.

The debismuthizing of lead has been the subject of a great deal of work and Dr. Kroll's contribution in this field is outstanding. Nevertheless, many points still remain to be cleared up, for this method of removing bismuth, if a thorough theoretical study is made of it, raises a number of related questions. As Dr. Kroll says, the problem of recovering by-products in refining has considerable commercial importance. But one cannot lay down hard and fast rules: different works are differently placed both technically and commercially, so that what is possible in one country is not so in another and a by-product which is difficult to treat in one works presents no problem to another which has the necessary facilities. For example, the de-antimonizing of solders by aluminium is systematically carried out in works having the means for the initial elimination of arsenic, without fear of danger in handling the dross.

In the same way we have confined ourselves to quoting methods which are applicable to normal economic conditions and not to a war economy, and for this reason certain interesting processes referred to by Dr. Kroll have not been mentioned in our paper.

We thank Dr. Kroll for his observations, which are the fruit of long experience, each point raised almost deserving a paper to itself.

* W. Kroll, *Metall u. Erz*, 1922, 19, 317.

FURTHER CORRESPONDENCE ON PAPER BY DR. E. VOCE: "THE RELATIONSHIP BETWEEN STRESS AND STRAIN FOR HOMOGENEOUS DEFORMATION."

(*J. Inst. Metals*, 1948, **74**, 537, 760.)

PROFESSOR FRANCESCO MAZZOLENI * (Member): In his reply to my communication on his paper (p. 769), Dr. Voce gives a diagram (Fig. H) in which are compared results obtained by the use of his own expression for the stress-strain relationship and those obtained by the use of the expression which I derived theoretically in 1941. In respect of my expression this diagram is quite wrong.

I have repeated the calculation, using the experimental data of Cook and Larke, with the results given in Table B.

TABLE B.

Strain (Cook and Larke)	1.05	1.10	1.20	1.30	1.40	1.50	1.60
Stress, tons/in. ² (Cook and Larke)	14.1	19.3	25.2	27.2	28.0	28.3	28.4
Calculated values, S_e	15.2	19.5	24.9	27.2	28.0	28.3	28.4

The values of S_e have been calculated from my equation :

$$S_e = S_1 \frac{a \left(\frac{L_0}{L} \right)^b}{1 + a \left(\frac{L_0}{L} \right)^b}$$

The coefficients a and b have the values 0.595 and 1.35, respectively, deduced from the diagram of $\ln \frac{S}{S_1 - S}$ against $\ln \frac{L_0}{L}$ drawn on the basis of Cook and Larke's experimental data (Fig. I, p. 1204).

The AUTHOR (*in reply*): In his analysis of Cook and Larke's curve for cupro-nickel, Professor Mazzoleni has confused percentage reduction in height under compression with percentage increase in length under tension. The percentage reduction in height, x , used by Cook and Larke is defined as :

$$x = \frac{100 (L_0 - L)}{L_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Therefore the deformation ratio, R , is given by :

$$R = \frac{L_0}{L} = \frac{1}{1 - \frac{x}{100}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Special Technology Department, Faculty of Engineering, University of Naples, Italy.

and not, as Professor Mazzoleni has assumed, by $1 + \frac{x}{100}$, which would, of course, be correct if x were the percentage increase in length under tension.

When the deformation ratio is properly determined and plotted against $\frac{S}{S_\infty - S}$ on a double logarithmic scale, the result is very far from a straight line, as shown by the insert to Fig. H of my reply to the original correspondence.

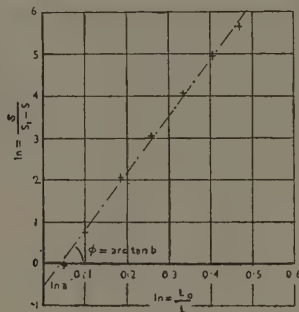


FIG. I.

In a private communication, Mr. J. H. Palm of the Nationaal Luchtvaart-laboratorium, Amsterdam, has pointed out an important weakness in Professor Mazzoleni's equation. It demands that the plastic modulus, or slope of the stress-strain curve, should rise to a maximum instead of falling continuously as experiment proves it to do.

Putting η equal to the logarithmic strain, so that $\eta = \ln \frac{L_0}{L}$, Professor Mazzoleni's equation can be written :

$$S = S_\infty \frac{a\epsilon^b\eta}{1 + a\epsilon^b\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Successive differentiations give :

$$\frac{dS}{d\eta} = S_\infty \frac{ab\epsilon^b\eta}{(1 + a\epsilon^b\eta)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\frac{d^2S}{d\eta^2} = S_\infty \frac{ab^2\epsilon^b\eta}{(1 + a\epsilon^b\eta)^3} (1 - a\epsilon^b\eta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now the plastic modulus, $\frac{dS}{d\eta}$, reaches a maximum* when the second

* That the point of inflection is a maximum and not a minimum is apparent from the fact that $\frac{d(1 - a\epsilon^b\eta)}{d\eta} = -ab\epsilon^b\eta$, which is negative for positive values of a and b .

From equation (6) $\epsilon^b\eta = 1/a$, and substitution of this in equations (4) and (3) shows that the maximum value of the plastic modulus is $bS_\infty/4$ and that it occurs when $S = S_\infty/2$.

differential coefficient becomes zero, that is to say when $(1 - a\epsilon^b\eta)$ becomes zero, since none of the other factors in equation (5) can do so. This condition is fulfilled when :

$$\eta_{(\text{max. slope})} = \frac{1}{b} \ln \frac{1}{a} (6)$$

Since a is less than unity, while both a and b are positive, it is evident from equation (6) that the maximum slope of Professor Mazzoleni's proposed stress-strain curve occurs at a definite strain part-way along it. This conclusion is in conflict with the weight of experimental evidence, which indicates a continuous decrease in the plastic modulus as the strain is increased. It therefore throws doubt on the validity of the assumptions on which Professor Mazzoleni's equation is based.

FURTHER CORRESPONDENCE ON PAPER BY MR. C. BLAZEY, MR. L. BROAD, MR. W. S. GUMMER, AND MR. D. B. THOMPSON: "THE FLOW OF METAL IN TUBE EX- TRUSION."

(*J. Inst. Metals*, this vol., pp. 163, 1025.)

MR. DANIEL R. HULL,* Ph.B. (Member): Although the authors have, with good reason, rejected the photograph as the best evidence of relative flow in various parts of the billet, I was prompted, on the appearance of their paper, to take a few photographs. If these do not indicate relative rates of flow, it seems to me that they do nevertheless indicate relative degrees of plastic motion, and are, therefore, pertinent.

All the billets used were of 70 : 30 brass. Fig. A (Plate CXXXVII) shows a partly extruded billet plus shell from a 1100-ton vertical Schloemann press, having a container and mandrel lubricated with oil and graphite, which leaves no skull. The original billet was $5\frac{7}{8}$ in. dia. by $8\frac{1}{2}$ in. long; the shell was $2\frac{5}{8}$ in. outside dia. by $\frac{3}{16}$ in. wall. The press was stopped about midway through the stroke, and the contents of the container were removed, sectioned lengthwise, etched, and photographed.

Fig. B (Plate CXXXVII) shows the product of the same press after completion of a normal operation. The whole cross-section of the billet appears to be flowing fairly uniformly into the die. The flow along the sloping face of the die is in agreement with Fig. 19 (p. 178 of the authors' paper), but the photograph reveals a movement down through the centre of the billet, along the mandrel, which Fig. 19 does not indicate. However, this movement hardly appears extensive enough to invalidate the authors' findings that: "the upper and lower parts of the shell . . . correspond with the upper and lower parts of the billet". It follows that the outside and inside portions of the billet would be found in corresponding portions of the shell wall.

Figs. C and D (Plate CXXXVII) represent billets 7 in. in dia. by 10 in. long, making a shell $2\frac{1}{2}$ in. outside dia. by $\frac{1}{4}$ in. wall, extruded in a 2200-ton horizontal Loewy press, with a dry container, leaving a skull. The sections were prepared in the same manner as those shown in Figs. A and B.

The difference between Fig. A and Fig. C is astonishing. In the latter, the whole mass of the billet is moving, except the small portion in the corner. It further appears that the outside portions are moving faster than the central portion, since recrystallization in the latter area is quite complete, whereas it has been only partly effected in the former. It seems to me that this surely indicates a difference in the amount of movement, with a strong probability that the rate of movement is involved. The whole agrees very well with the authors' Figs. 4 and 5 (p. 169 of the paper).

Figs. E and F (Plate CXXXVIII) are photomicrographs taken respectively at points A and B in Fig. D. While they are irrelevant to the subject of metal flow, it is worth while calling attention to the grain growth that has occurred in the shell. This could hardly take place while the metal was in plastic

* Assistant Technical Manager, American Brass Co., Waterbury, Conn, U.S.A.



FIG. D.—Same as Fig. C, after Completion of Stroke.

FIG. C.—Vertical Section of a 70 : 30 Brass Billet Partly Extruded in a Non-Lubricated Container. Horizontal 2200-ton Loewy press.

FIG. B.—Same as Fig. A, after Completion of Operation.

FIG. A.—Vertical Section of a 70 : 30 Brass Billet Partly Extruded in a Lubricated Container. Vertical 1100 - ton

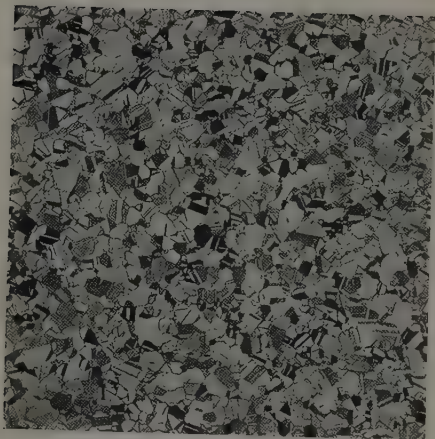


FIG. E.—Grain-Size in Throat of Die at *A* in Fig. D. $\times 75$.



FIG. F.—Grain-Size in Shell at *B* in Fig. D. $\times 75$.

motion, in the container; nevertheless, on emergence, a grain-size consistent with the temperature was attained.

Then there is the question of the shape of the die entrance: in the authors' paper, and in Figs. A and B, it slopes steeply from the outside, while in Figs. C and D, there is a considerable flat bearing before the entrance slope begins. Figs. A and B show the metal moving down along this slope, and into the die. Thus, there is no unworked metal in the outside corner. The metal at that point has apparently been in motion throughout the operation. In the end, the discard remaining must have come from the back end of the billet. From Figs. C and D, on the other hand, it may be inferred that the unworked crystals represent metal that has never moved, while the main mass of the billet has flowed past it.

The shape of the die entrance, as well as the cross-sectional area of the shell in relation to that of the billet, may be expected to have an influence on flow, but it would be a minor factor compared to the friction between the billet and the container.

In the work with tubes there appears only a slight indication of the differential flow between the surface and the centre of the billet, which results in a core defect when rods are extruded in a dry container, without leaving a skull.

The AUTHORS (*in reply*): We are pleased to have some of our results confirmed by Mr. Hull, especially as he used a large horizontal press in one experiment and so checked our results with two vertical presses.

We etched all our sections, but did not use photographs to illustrate the paper mainly because of the difficulty of revealing the thin drawn-out pins close to and below the level of the die.

Although Fig. 19 of our paper does not show flow in an area close to the mandrel, Fig. 17, which resembles Mr. Hull's Fig. A, does show that there is disturbance of the metal in this region. Mr. Hull's Fig. B, taken at the completion of the stroke, indicates that the disturbance is probably restricted to the early and middle stages of extrusion.

The finely crystalline, almost vertical, band of metal shown in Mr. Hull's Fig. C is probably composed largely of the middle horizontal half of the billet, and the incompletely recrystallized region at the left nearer the mandrel is probably composed largely of the top quarter of the billet. When Fig. C is compared with our Figs. 6 and 7, the mode of flow may be more easily understood. Figs. 6 and 7 show that the central part of the billet does move rapidly and that the top and bottom quarters move more slowly.

With regard to die angle, the effect of steep angles up to 60° has not yet been determined by us. Steep angles may reduce or even prevent the formation of "dead" metal in the bottom corner even in a non-lubricated container. In a non-lubricated container we invariably obtained un-recrystallized metal at the bottom outer corners in partly and fully extruded billets, using dies with an included angle of 130° similar to those shown in Mr. Hull's Fig. A.

Although, as Mr. Hull states in his final paragraph, there is only a slight indication in tube extrusion of the "defect" often found in rod extrusion, that indication seems to appear as blistering in the shell when a lubricated disc is used. We are also inclined to think that the too-free use of lubricant on the mandrel can lead to the same trouble through an accumulation of excess lubricant between the top of the billet and disc by a stripping action during the piercing stroke.

We agree with the implication in Mr. Hull's contribution that much remains to be done in this study of flow.

OBITUARY

JOHN HENRY GILL MONYPENNY.

The death occurred at Sheffield on 2 March 1949 of Mr. J. H. G. Monypenny, who for more than forty years had been closely associated with Brown Bayley's Steel Works, Ltd.

Mr. Monypenny was born in 1885 and received the early part of his education at the Royal Grammar School, Sheffield. He then gained a technical scholarship to study metallurgy at the University College, Sheffield, and before leaving there was awarded an Associateship in Metallurgy and the Mappin Medal of the University. In 1904, Mr. Monypenny joined the staff of Brown Bayley's Steel Works, Ltd., and for nearly twenty-five years had charge of the firm's research laboratory, for the development of which he was largely responsible. His work there was directed mainly to the investigation of stainless steels, and an account of many of the researches which he conducted is given in his book on "Stainless Iron and Steel", the first edition of which appeared in 1926. In 1928, Mr. Monypenny became technical representative of Brown Bayley's Steel Works, Ltd., in which position he continued until his retirement in 1946.

Throughout his career Mr. Monypenny made many valuable contributions to learned societies in this country and in America. He was elected a member of the Institute of Metals in 1919 and was Chairman of the Sheffield Local Section from 1927 to 1929. He was, of course, a member of the Iron and Steel Institute and served on its Corrosion and Alloy Steels Research Committees. He was a Fellow of the Institute of Physics, a Fellow of the Institution of Metallurgists, a member of the American Institute of Mining and Metallurgical Engineers, and of the American Society for Metals. In addition, Mr. Monypenny served for some years on the Council of the Faraday Society, and from 1935 to 1938 was Chairman of the British Chemical Plant Manufacturers' Association.

WILLIAM FREDERICK ROWDEN.

The death occurred at Hatch End, Middlesex, on 17 March 1949, after a long illness, of Mr. W. F. Rowden, the well-known authority on the development of alloy steels.

Born on 30 May 1897, Mr. Rowden spent his early days at the Openshaw Works of Messrs. Sir W. G. Armstrong Whitworth and Co., Ltd. In 1930 he joined High Speed Alloys, Ltd., Widnes, as technical adviser, and in this capacity he maintained contact with almost all the metallurgists of the country who were concerned with the use of alloy elements for steelmaking.

In April 1937 he joined the staff of the Development and Research Department of The Mond Nickel Co., Ltd. He left Mond Nickel at the end of 1938 to head the European force of the Climax Molybdenum Company, becoming a director of Climax Molybdenum Company of Europe, Ltd.

During the war he rendered valuable service as a metallurgical adviser to the Department of Tank Design, Ministry of Supply. He maintained a close liaison with American practice, and made frequent journeys to the U.S.A., where he had many friends.

He took a prominent part in the work of scientific and technical associa-

tions; in addition to his membership of the Institute of Metals, which he joined in 1945, Mr. Rowden was a member of the Iron and Steel Institute, the Institute of British Foundrymen, the Institute of Welding, the Manchester Association of Engineers, and the Manchester Metallurgical Society.

ERNEST ALFRED SMITH, A.R.S.M.

Mr. E. A. Smith died after a short illness at his home in Hastings on 7 April 1949, aged 81.

Ernest Alfred Smith was born in London and was educated at the North London Collegiate School. He was the second son of Richard Smith, who was associated with Dr. Percy for so many years at the Royal School of Mines. Ernest Smith entered the Royal School of Mines in 1885 and graduated A.R.S.M. in 1888.

His first post was in the City of London, with Mr. Kitto, Chemist and Assayer, from which he was called in 1890 to fill an emergency gap as Lecturer in Metallurgy and Assaying at the Royal College of Science, Dublin, during the illness of Professor Hartley. On returning from Dublin he was appointed to the Royal School of Mines staff under Professor Roberts-Austen. In 1895 he was again called upon to deputize for Professor Hartley in Dublin for a time.

It is of passing interest to note that in 1897 he was runner-up to Thomas Turner for the new professorship of metallurgy at Mason College, Birmingham. Instead he was appointed in 1898 to the Assay Office, Sheffield, as Deputy Assay Master, where he served for over 20 years. Mr. Smith then became the first secretary of the British Non-Ferrous Metals Research Association when that body was established in offices in Temple Row, Birmingham, in 1920. Later he returned to the precious metal field with the Sheffield Smelting Company and subsequently (1932) with Oakes, Turner, and Co. (an associate company of Johnson, Matthey and Co., Ltd.), also in Sheffield. He retired in 1939 and moved south again, to Hastings, largely on account of his wife's health.

Of the five books which he wrote, the first was "Dental Metallurgy", produced at the request of students. It became widely known and its sixth edition was published in 1947. There followed: "The Zinc Industry", "The Platinum Metals", "Working in Precious Metals", and "The Sampling and Assay of the Precious Metals", of which latter reference book a new edition also appeared in 1947.

Mr. Smith was an Original Member of the Institute of Metals and contributed several papers to its *Journal*. He also presented many papers to other scientific societies and to the technical press over a period of 50 years, his last contributions being as recent as January 1949; and he lectured to various trade societies in London, Birmingham, and Sheffield. He had a deep interest in the noble metals and their manipulation, both in modern times and in antiquity. Mr. Smith was the first Freeman and Silver Medallist of the Silver Trades Technical Society, and was honorary scientific adviser to the Birmingham Jewellers' Association, for which he carried out several investigations. For many years he was a Fellow of the Chemical Society, a member of the Society of Chemical Industry, and a member of the Institution of Mining and Metallurgy.

A firm Congregationalist, Mr. Smith was for many years Superintendent of the Broompark Mission Sunday School, Sheffield, and on repeated occasions was both Secretary and Treasurer of Endcliffe Park Chapel. Later he became a deacon of Broompark Church; and even after retiring he undertook, under war-time pressure, the secretaryship of Robertson Street Congregational Church, Hastings.

Mr. Smith leaves two daughters and two sons; both of the latter have followed the family metallurgical interest, and are also members of the Institute of Metals.

ARTHUR TITLEY.

Mr. Arthur Titley, an Original Member of the Institute of Metals, died at his home at Four Oaks, Sutton Coldfield, on 19 December 1948, aged 85 years.

Born in Birmingham, Mr. Titley served his apprenticeship, from 1881 to 1885, with Messrs Samuel Fisher and Co., Nile Foundry; subsequently he served as a draughtsman with this firm, with Messrs. Morewood and Co., Smethwick, and with other firms. In 1905 he started a consulting practice in Birmingham with Mr. Charles H. Wall, which lasted until his retirement in 1932.

His work in connection with plant for metal rolling and drawing and general engineering led Mr. Titley to take an interest in the history of engineering and he was responsible for founding the Newcomen Society on the occasion of the centenary of the death of James Watt in 1919. He was first President of the Society (1920-22), and to mark its coming of age he was elected for a further period of office in 1942-43.

Mr. Titley collaborated with Dr. H. W. Dickinson in 1933 to write a volume to commemorate the centenary of Trevithick's death: "Robert Trevithick, the Engineer and the Man"; he also collaborated in editing in 1938 "John Smeaton's Diary of His Journey to the Low Countries in 1755".

Mr. Titley was one of the oldest members of the Institution of Mechanical Engineers, having been elected in 1890.

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Monograph No. 5: "Symposium on Internal Stresses in Metals and Alloys". (Papers No. 1072-1107.)

Monograph No. 7: "The Solidification of Castings: A Review of the Literature", by R. W. Ruddle, M.A., A.I.M. (Paper No. 1206.)

Monograph No. 8: "Metallurgical Applications of the Electron Microscope". (Papers No. 1193-1205.)

N.B. **Monograph No. 6:** "Symposium on Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working" contains only material reprinted from the present volume of the *Journal* (pp. 285-390 and 1048-1101).

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